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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to laminating mold photovoltaic cells formed by carrying out the laminating of the configuration component of the pin junction which has p type layer which consists of a silicon system non-single crystal semiconductor, i type layer, and n type layer more than 3 configuration component at least, such as a solar battery and a sensor.

[0002]

[Description of the Prior Art] The photovoltaic cell which is an optoelectric transducer which changes sunlight into electrical energy is widely applied as noncommercial power sources for small power, such as a calculator and a wrist watch, and will attract attention in the future as a technique usable as the so-called power for an alternative of fossil fuels, such as petroleum and coal.

[0003] It is a technique using the photoelectromotive force of the pn junction of a semi-conductor, and a photovoltaic cell absorbs sunlight and generates the optical carrier of an electron and an electron hole, and semi-conductors, such as silicon, carry out the drift of the optical carrier by the internal field of the pn junction section, and take it out outside.

[0004] Production of such a photovoltaic cell is performed by mainly using a semi-conductor manufacture process. The single crystal of the silicon which carried out valence-electron control by crystal growth methods, such as a CZ process, at p mold or n mold is specifically produced, this single crystal is sliced and a silicon wafer with a thickness of about 300 micrometers is produced. Furthermore, a valence-electron control agent is diffused so that it may become a conductivity type opposite to a wafer, and pn junction is produced by carrying out the laminating of the layer of a conductivity type of a different kind.

[0005] By the way, although single crystal silicon is adopted as the main photovoltaic cells put in practical use from a viewpoint of current, dependability, or photoelectric conversion efficiency, in order to use a semi-conductor manufacture process for production of a photovoltaic cell as mentioned above, the manufacturing cost is increasing.

[0006] Since single crystal silicon is indirect transition, other faults of a single-crystal-silicon photovoltaic cell have a small light absorption multiplier, and they are having to create in thickness of at least 50 micrometers in order to absorb more sunlight, a band gap's being about 1.1eV, and being unable to use a part for short wave Naganari effectively, since [ suitable as a photovoltaic cell ] it is narrower than 1.5eV.

[0007] Even if it reduces a manufacturing cost using polycrystalline silicon, the problem of an indirect transition can remain and cannot decrease thickness of a photovoltaic cell. Moreover, polycrystalline silicon also has the problem of a grain boundary and others.

[0008] Furthermore, although it is a crystalline substance therefore, a wafer with a big area cannot be manufactured. Wiring for acting serialization or parallelization as a unit element child large-area-izing being difficult and taking out large power must be performed, Moreover, since expensive mounting is needed in order to protect a photovoltaic cell from the mechanical damage brought about according to

various meteorological conditions, in case it is used outdoors, there is a problem that the manufacturing cost to the amount of unit generations of electrical energy will become comparatively high-priced compared with the existing generation-of-electrical-energy approach.

[0009] From such a situation, in advancing utilization as an object for the power of a photovoltaic cell, low-cost-izing and large area-ization are important technical problems, various examination is made and the ingredient pursuit of the ingredient of low cost, an ingredient with high photoelectric conversion efficiency, etc. is performed.

[0010] As an ingredient of such a photovoltaic cell, the compound semiconductor of III(s), such as II(s), such as the amorphous semiconductor of tetra-HEDORARU systems, such as amorphous silicon and amorphous silicon germanium and amorphous silicon carbide, and CdS, Cu<sub>2</sub>S, VI group, and GaAs, GaAlAs, and V group etc. is mentioned. The thin film photovoltaic cell which used the amorphous semiconductor for the photoelectromotive-force generating layer has the advantages, like that thickness is thin and ends and it can deposit [ that the film of a large area can be created as compared with a single crystal photovoltaic cell, or ] on the substrate ingredient of arbitration, and promising \*\* is especially carried out.

[0011] However, as a component for power, as for the photovoltaic cell using the above-mentioned amorphous semiconductor, the between title remains in respect of improvement in photoelectric conversion efficiency, and improvement in dependability.

[0012] Narrowing a band gap and increasing the sensibility to the light of long wavelength, for example as a means of improvement in the photoelectric conversion efficiency of the photovoltaic cell using an amorphous semiconductor, is performed. namely, amorphous silicon -- a band gap -- about about 1.7eV -- it is -- a long wave 700nm or more -- since merit's light cannot be absorbed and it cannot use effectively -- a long wave -- it is examined that the band gap which has sensibility to Nagamitsu adopts a narrow ingredient.

[0013] The amorphous silicon germanium with which even about 1.7eV can change a band gap from 1.3eV grade to arbitration easily as such an ingredient by changing the ratio of the silicon material gas at the time of membrane formation and germanium material gas is mentioned.

[0014] Moreover, using the so-called stack cel which carries out two or more laminatings of the photovoltaic cell of unit element child structure as other approaches of raising the photoelectric conversion efficiency of a photovoltaic cell is indicated by the U.S. Pat. No. 2949498 number. although the pn junction crystal semi-conductor is used for this stack cel -- that thought -- an amorphous substance or a crystalline substance -- it is common in all, a sunlight spectrum is made to absorb efficiently by the photovoltaic cell of a different band gap, and generating efficiency is raised by increasing Voc.

[0015] A stack cel carries out two or more laminatings of the configuration component of a different band gap, and it raises conversion efficiency by absorbing each part of the spectrum of sunrays efficiently, and it is designed so that the band gap of the so-called bottom layer located in the bottom of it rather than the band gap of the so-called top layer located in the optical incidence side of the configuration component which carries out a laminating may become narrow.

[0016] By this The spectrum of sunrays Fully absorbed and photoelectric conversion efficiency has been improved by leaps and bounds (88 KMiyachi-et.al. and Proc. 11th E.C. Photovoltaic-Solar-Energy-Conf. Montreux, Switzerland, 1992). KNomoto et.al. -- "a-Si-Alloy-Tree-Stacked-Solar-Cells-with-High-Stabilized-Efficiency", 275 7 th-Photovoltaic-Science-and-Engineering-Conf. Nagoya, 1993.

[0017]

[Problem(s) to be Solved by the Invention] By the way, since the above-mentioned photovoltaic cell was a component which used the amorphous semiconductor for all the i type layers, there was a limitation in reduction of the so-called photodegradation to which photoelectric conversion efficiency falls by optical exposure. Membraneous quality deteriorates by optical exposure, the performance traverse of a carrier is not caused by worsening and amorphous silicon and amorphous silicon germanium of this are phenomena peculiar to an amorphous semiconductor which are not looked at by crystal system. Therefore, when using for a power application, it is inferior to dependability and the actual condition has

been the failure of utilization.

[0018] Moreover, research is done in recent years also about the stack cel of an amorphous system / not only amorphous system but an amorphous system / crystalline substance system. Improvement in the photoelectric conversion efficiency of a photovoltaic cell is reported. (It Hamakawa(s).) Y-etc. "Device-Physics-and-Optimum-Design-of-a-Si/Poly-Si-Tandem-Solar-Cells", Proceedings-of and 4 th-International-PVSEC, pp.403-408, Feb.1989., A. -- Shah, H.Keppner, and etc. -- "Intrinsic-Microcrystallins-Silicon(muc-Si:H)-A-Promising-New-Thin-Film-Solar-Cell-Material"IEEE-First-World-Conference-on-Ph otovoltaic-Energy-Conversion, pp.409-412, Dec.1994, Mitchell and R.L.etc. - - "The-DOE/SERI-Poly-crystalline-Thin-Film-Subcontract-Program, "Proceedings-of and 20 th-IEEE-Photovoltaic-Specialists-Conference, PP.1469-1476, Sept.1988.

[0019] However, when the balance of the optical generation-of-electrical-energy current of a stack cel was taken into consideration, it was not what must thicken thickness of the cel by the side of optical incidence (large band gap side), and may fully be satisfied from a viewpoint of photodegradation.

[0020] Therefore, it is requested that the further reduction of the photodegradation of an amorphous photovoltaic cell and the photoelectric conversion efficiency after photodegradation are raised. Furthermore, in order to use for a power application, the further improvement in photoelectric conversion efficiency is called for.

[0021] This invention aims to let dependability offer a laminating mold photovoltaic cell with high photoelectric conversion efficiency highly, though it is practical low cost.

[0022]

[Means for Solving the Problem] In the laminating mold photovoltaic cell which carried out two or more laminatings of the configuration component of the pin junction which has p type layer which this invention becomes from a silicon system non-single crystal semiconductor, i type layer, and n type layer that the above-mentioned purpose should be attained It counts from an optical incidence side and microcrystal silicon is used as an i type layer of the third pin junction, using microcrystal silicon as an i type layer of the second pin junction, using amorphous silicon as an i type layer of the first pin junction.

[0023] As for the thickness of the microcrystal silicon which is i type layer of the second pin junction, it is desirable that it is the 0.5-micrometer or more range of 1.5 micrometers or less.

[0024] As for the thickness of the microcrystal silicon which is i type layer of the third pin junction on the other hand, it is desirable that it is the 1.5-micrometer or more range of 3.5 micrometers or less.

[0025] Moreover, the microcrystal silicon which is i type layer of the second pin junction contains boron, and, as for the boron content, it is desirable that it is 8 ppm or less.

[0026] On the other hand, the microcrystal silicon which is i type layer of the third pin junction contains boron, and, as for the boron content, it is desirable that it is 8 ppm or less.

[0027] Furthermore, it is desirable that n type layer of the second pin junction consists of a bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon.

[0028] It is desirable that n type layer of the third pin junction consists of a bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon on the other hand.

[0029] And it is desirable that the light absorption multiplier of 950nm of the microcrystal silicon which is i type layer of the second and third pin junction is one or more [ 200cm - ].

[0030] Moreover, it is desirable that the microcrystal silicon which is i type layer of the second pin junction is formed by the microwave plasma-CVD method.

[0031] Also as for the microcrystal silicon which is i type layer of the third pin junction on the other hand, being formed by the microwave plasma-CVD method is desirable.

[0032] Furthermore, as for the laminating mold photovoltaic cell of this invention, it is desirable to be formed by the roll-to-roll process which carries out a laminating, building over and conveying a long substrate between the rolls of a pair.

[0033] As mentioned above, this invention relates to a new laminating mold photovoltaic cell, and explains a configuration and an operation of this invention further below.

[0034] this invention person etc. acquired the following knowledge, as a result of conquering the technical problem mentioned above and photodegradation's examining wholeheartedly a laminating

mold photovoltaic cell with high photoelectric conversion efficiency few.

[0035] In order to reduce the rate of photodegradation and to raise the photoelectric conversion efficiency after photodegradation, maintaining high photoelectric conversion efficiency Also in a laminating mold photovoltaic cell, count from an optical incidence side and amorphous silicon is used as an i type layer of the first pin junction. The laminating mold photovoltaic cell, i.e., the photovoltaic cell of the triple mold of a-Si/ $\mu$ c-Si/ $\mu$ c-Si, using microcrystal silicon as an i type layer of the third pin junction is suitable, using microcrystal silicon as an i type layer of the second pin junction.

[0036] moreover, the thing which it separates from the thickness considered to be conventionally suitable in the thickness of the microcrystal silicon which is i type layer of the second pin junction, and is made thin -- or/and, by separating from the thickness considered to be conventionally suitable in the thickness of the microcrystal silicon which is i type layer of the third pin junction, and making it thin, also in the photovoltaic cell of a stack mold, photodegradation can be controlled further and the conversion efficiency after photodegradation can be raised.

[0037] furthermore, the thing for which the microcrystal silicon which is i type layer of the second pin junction contains boron, and sets the content to 8 ppm or less -- or/and, when the microcrystal silicon which is i type layer of the third pin junction contains boron and sets the content to 8 ppm or less, also in a laminating mold photovoltaic cell, photodegradation can be controlled further and maintenance \*\*\*\*\* can do high photoelectric conversion efficiency.

[0038] And when n type layer of the second pin junction is formed of the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon The microcrystal silicon of i type layer formed on n type layer when n type layer of the third pin junction is formed of the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon by or/and, the quick rate of sedimentation And while being able to form good microcrystal silicon and being able to control photodegradation, high photoelectric conversion efficiency is maintainable.

[0039] Moreover, even when the light absorption multiplier of 950nm of the microcrystal silicon which is i type layer of the second and third pin junction is one or more [ 200cm - ], and thickness of microcrystal silicon is made thin, high photoelectric conversion efficiency can be maintained.

[0040] Furthermore, as a deposition means of microcrystal silicon, the gas decomposition effectiveness of material gas is high, when also whenever [ high vacuum ] controls especially the plasma state in early stages of deposition using the microwave (0.1-10GHz) CVD method in which maintaining a discharge is possible, localized level density can be controlled, good membraneous quality can be maintained, and the photoelectric conversion efficiency after the photodegradation of the photovoltaic cell of the above-mentioned triple mold can be raised more.

[0041] concrete -- as i type layer of the second pin junction -- microcrystal silicon -- using -- as i type layer of the third pin junction -- microcrystal silicon -- \*\*\*\* -- in the photovoltaic cell of an amorphous system stack mold, an improvement of the semi-conductor layer whose photodegradation was large is made by things, and photodegradation can be further controlled also in the photovoltaic cell of a stack mold by them.

[0042] Moreover, by using microcrystal silicon as an i type layer of the third pin junction, carrying out light absorption until now can carry out light absorption also of the comparatively difficult long wavelength light, it can have a higher short-circuit current also in the photovoltaic cell of a stack mold, and high photoelectric conversion efficiency can be maintained.

[0043] Furthermore, by separating from the thickness considered to be conventionally suitable in the thickness of the microcrystal silicon which is i type layer of the second pin junction, or/and the thickness of the microcrystal silicon which is i type layer of the third pin junction, and making it thin, the increment in the localized level in the inside of i type layer by optical exposure can be controlled, and photodegradation can be controlled more also in the photovoltaic cell of a stack mold.

[0044] And by the microcrystal silicon which is i type layer of the second pin junction containing boron, and setting the content as 8 ppm or less Or/and, by the microcrystal silicon which is i type layer of the third pin junction containing boron, and setting the content as 8 ppm or less By not checking growth of microcrystal silicon and its microcrystal, and improving the performance traverse of the hole at the time

of an optical generation of electrical energy, photodegradation can be controlled and high photoelectric conversion efficiency can be maintained.

[0045] Moreover, when n type layer of the second pin junction is formed of the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon Or/and, when n type layer of the third pin junction is formed of the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon The microcrystal silicon of i type layer formed on n type layer can be formed by the quick rate of sedimentation, good microcrystal silicon with few impurities is formed, and high photoelectric conversion efficiency with little photodegradation can be maintained.

[0046] Furthermore, when the light absorption multiplier of 950nm of the microcrystal silicon which is i type layer of the second and third pin junction is one or more [ 200cm - ] The thickness of the microcrystal silicon which is i type layer of the second and third pin junction It can separate from the thickness considered to be conventionally suitable, and can be made thin, the increment in the localized level in the inside of i type layer by optical exposure can be controlled, and photodegradation can be controlled more also in the photovoltaic cell of a stack mold. And carrying out light absorption until now can also absorb the light of the comparatively difficult long wavelength, and the higher photoelectric conversion efficiency also in the photovoltaic cell of a stack mold can be maintained.

[0047] Moreover, by forming the microcrystal silicon which is i type layer of the second and third pin junction by the microwave plasma-CVD method, the material gas by which hydrogen dilution was carried out in large quantities can be decomposed efficiently, and it can be activated, and even if it is the quick rate of sedimentation, the low good microcrystal silicon of defect density can be obtained.

[0048] Furthermore, if the laminating mold photovoltaic cell of this invention is formed with a roll-to-roll process, productivity can be raised extremely.

[0049] By the above laminating mold photovoltaic cells of this invention, photodegradation can be controlled, the rate of photodegradation can be reduced, maintaining high photoelectric conversion efficiency, and the photoelectric conversion efficiency after photodegradation can be raised.

[0050]

[Embodiment of the Invention] Although the suitable operation gestalt of the laminating mold photovoltaic cell of this invention is explained below, this invention is not restricted to this operation gestalt.

[0051] this invention person etc. performed the following examination, in order to raise further the photoelectric conversion efficiency of the photovoltaic cell of a non-single-crystal-silicon system, to prevent photodegradation and to raise the dependability of the photovoltaic cell of a non-single-crystal-silicon system.

[0052] First, in order to reduce photodegradation, it is like common knowledge that it is effective to constitute a photovoltaic cell in a stack mold. However, it could not say that reduction of photodegradation was still enough, but this invention person etc. acquired the following knowledge, as a result of having advanced examination of the configuration of the photovoltaic cell of a stack mold.

[0053] That is, also in the photovoltaic cell of a stack mold, rather than the photovoltaic cell of the double mold which carried out 2 laminatings of the pin junction, I hear that the photovoltaic cell of the triple mold which carried out 3 laminatings of the pin junction can reduce photodegradation more, and there is. When the semiconductor material of the same class is used, the optical generation-of-electrical-energy current of this which the direction of a triple mold generates in the pin junction per one becomes less than a double mold, and it is considered to be because for the recombination of the electron hole leading to the photodegradation of an amorphous semiconductor and an electron to decrease.

[0054] Moreover, also in the photovoltaic cell of a triple mold, it counted from the optical incidence side and the knowledge that the laminating mold photovoltaic cell, i.e., the photovoltaic cell of the triple mold of a-Si/ $\mu$ c-Si/ $\mu$ c-Si, using microcrystal silicon as i layers of the third pin junction was most suitable for reduction of photodegradation was acquired, using microcrystal silicon as i layers of the second pin junction, using amorphous silicon as an i type layer of the first pin junction. This is because photodegradation can be reduced more rather than an old non-single-crystal-silicon system triple mold photovoltaic cell by using the microcrystal silicon whose light absorption multiplier of 950nm is one or

more [ 200cm - ], using microcrystal silicon as an i type layer of the pin junction of the second and third  
\*\*.

[0055] Then, this invention person etc. advanced examination further about the photovoltaic cell of the triple mold of a-Si/ $\mu$ c-Si/ $\mu$ c-Si. Consequently, in order to have made the highest photoelectric conversion efficiency of the photovoltaic cell of the triple mold of a-Si/ $\mu$ c-Si/ $\mu$ c-Si, it turned out that it is suitable to set to 1.90eV the band gap of the amorphous silicon which is i type layer of the first pin junction from 1.60eV, to set to 0.5 micrometers or more 1.5 micrometers or less thickness of the microcrystal silicon which is i type layer of the second pin junction, and to make or less [ 1.5 micrometers or more ] into 3.5 thickness of the microcrystal silicon which is i type layer of the third pin junction.

[0056] At this time, the thickness of amorphous silicon which is i type layer of the second pin junction had desirable 500-2500Å, and it turned out that it is 700-1500Å more preferably.

[0057] Moreover, it turned out that the light absorption multiplier of 950nm of the microcrystal silicon which is i type layer of the second and third pin junction is one or more [ 200cm - ]. (Hereafter, a "top cel" and the second pin junction are written as a "middle cel", and the third pin junction is written for the first pin junction as a "bottom cel".)

Furthermore, it examined reducing the rate of photodegradation, i.e., making photoelectric conversion efficiency (it being hereafter described as "stabilization conversion efficiency".) after decline in the photoelectric conversion efficiency by photodegradation is saturated into max, this invention person etc. having advanced examination and maintaining high photoelectric conversion efficiency in consideration of both the photoelectric conversion efficiency of the photovoltaic cell of the triple mold of a-Si/ $\mu$ c-Si/ $\mu$ c-Si, and the rate of photodegradation.

[0058] As greatly [ since it is the configuration which carried out series connection of two or more pin junction / the current value generated in each pin junction ] as possible, if each current value is not near, high photoelectric conversion efficiency will not be acquired by the photovoltaic cell of a stack mold.

[0059] Therefore, if thickness of the microcrystal silicon which is i type layer of the middle cel of the photovoltaic cell of the triple mold of a-Si/ $\mu$ c-Si/ $\mu$ c-Si is made thinner than 0.5 micrometers, there will be too few currents generated by light, and the photoelectric conversion efficiency as a triple cel will fall. On the other hand, if the thickness is thicker than 1.5 micrometers, the current of a middle cel is enough, but since the quantity of light which enters into a bottom cel becomes less, there will be too few currents which a bottom cel generates, and the photoelectric conversion efficiency as a triple cel will fall.

[0060] Moreover, if thickness of the microcrystal silicon which is i type layer of a bottom cel is made thinner than 1.5 micrometers, there will be too few currents generated by light, and the photoelectric conversion efficiency as a triple cel will fall. On the other hand, if the thickness is thicker than 3.5 micrometers, it will have a bad influence also on the phototaxis of the carrier at the time of an optical generation of electrical energy, FF (curvilinear factor) of a bottom cel will be reduced, and the photoelectric conversion efficiency as a triple cel will fall.

[0061] As a result of repeating such examination, the thickness of the microcrystal silicon as an i type layer of a middle cel was understood that 0.5-micrometer or more thing for which 1.5 micrometers or less are more preferably set to 0.6 micrometers or more 1.2 micrometers or less is desirable.

[0062] Moreover, the thickness of the microcrystal silicon as an i type layer of a bottom cel was understood that 1.5-micrometer or more thing for which 3.5 micrometers or less are more preferably set to 1.7 micrometers or more 3.3 micrometers or less is desirable.

[0063] Furthermore, high photoelectric conversion efficiency was able to be maintained by controlling deterioration of the membrane quality by superfluous inactive boron, and improving the performance traverse of the hole at the time of an optical generation of electrical energy further, controlling photodegradation, without checking growth of the microcrystal of microcrystal silicon by having set to 8 ppm or less the content of the boron contained in the microcrystal silicon which is i type layer of a middle cel.

[0064] In addition, the microcrystal silicon which is i type layer of a bottom cel was also able to

maintain high photoelectric conversion efficiency by controlling deterioration of the membraneous quality by superfluous inactive boron, and improving the performance traverse of the hole at the time of an optical generation of electrical energy further, controlling photodegradation, without checking growth of the microcrystal of microcrystal silicon by having set to 8 ppm or less similarly the content of the boron contained in microcrystal silicon.

[0065] Moreover, by forming n type layer of a middle cel by the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon The microcrystal silicon of i type layer formed on n type layer can be formed by the quick rate of sedimentation, mixing of an impurity can be controlled as much as possible, and good microcrystal silicon can be formed, Moreover, the thing for which the microcrystal silicon of i type layer formed on n type layer is formed as good microcrystal silicon with few amorphous components from the early stages of deposition, Furthermore, by forming a n-type-semiconductor layer by the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon It becomes possible to deposit the microcrystal silicon of i type layer at temperature comparatively higher than the deposition substrate temperature examined so far, and better microcrystal silicon can be formed, In addition, by forming n type layer by the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon By the damage to n type layer by the hydrogen ion in early stages of [ deposition ] the microcrystal silicon of i type layer etc. being mitigable etc., high photoelectric conversion efficiency with little photodegradation was maintainable.

[0066] Furthermore, by forming n type layer of a bottom cel by microcrystal silicon or microcrystal silicon, amorphous silicon, and the bilayer The microcrystal silicon of i type layer formed on n type layer can be formed by the quick rate of sedimentation, mixing of an impurity can be controlled as much as possible, and good microcrystal silicon can be formed, Moreover, the thing for which the microcrystal silicon of i type layer formed on n type layer is formed as good microcrystal silicon with few amorphous components from the early stages of deposition, Furthermore, by forming n type layer by the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon It becomes possible to deposit the microcrystal silicon of i type layer at temperature comparatively higher than the deposition substrate temperature examined so far, and better microcrystal silicon can be formed, In addition, by forming n type layer by the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon By the damage to n type layer by the hydrogen ion in early stages of [ deposition ] the microcrystal silicon of i type layer etc. being mitigable etc., high photoelectric conversion efficiency with little photodegradation was maintainable.

[0067] Moreover, even if it was the case where thickness of the microcrystal silicon which is i type layer of a bottom was made thin even to the above values, by enlarging the light absorption multiplier of microcrystal silicon showed that the current value generated at a bottom was maintainable.

[0068] Furthermore, even if it was the case where thickness of the microcrystal silicon which is i type layer of a bottom was made thin even to the above values, by making the light absorption multiplier of 950nm of microcrystal silicon or more [ 200cm - ] into one showed that the current value generated at a bottom was maintainable.

[0069] By specifically making into an elevated temperature deposition substrate temperature of the microcrystal silicon which is i type layer of a bottom, or changing a hydrogen dilution ratio showed that the current value generated at a bottom was maintainable.

[0070] Moreover, by using microcrystal silicon for i type layer of a bottom with middle, the open end electrical potential difference (Voc) which had become a problem until now could be enlarged comparatively, and high photoelectric conversion efficiency was able to be maintained.

[0071] Furthermore, it has the work which mainly raises the open end electrical potential difference (Voc) of a photovoltaic cell by arranging an amorphous silicon layer or an amorphous silicon carbon layer between p layers and microcrystal silicon layers of a middle cel and a bottom cel. This is considered because the diffusion potential of pin junction becomes large by an amorphous silicon layer or the amorphous silicon carbon layer. Moreover, forming the obstruction with which the electron generated by light in microcrystal silicon prevents being spread in p layers is also considered.

[0072] The thickness of an amorphous silicon layer or an amorphous silicon carbon layer has 50Å -



more preferably desirable 350Å - 450Å. Moreover, even if it had arranged the amorphous silicon layer or amorphous silicon carbon layer of thickness of this level, the rate of photodegradation of a photovoltaic cell hardly increased.

[0073] Furthermore, this invention person etc. was able to get good microcrystal silicon with little defect density wholeheartedly by forming microcrystal silicon and optimizing formation conditions further by the microwave (0.1-10GHz) plasma-CVD method, as a result of research. Consequently, the photoelectric conversion efficiency of the photovoltaic cell which used microcrystal silicon for i type layer could be raised, and the rate of photodegradation also fell. Therefore, the ballast factor was able to be raised.

[0074] To having formed microcrystal silicon conventionally, using RF plasma-CVD method for almost, this forms microcrystal silicon by the microwave plasma-CVD method, and can attain it by optimizing formation conditions further. It is thought that the reason was able to form good microcrystal silicon since the mobility of the precursor in the growth front face of the thin film deposited that the decomposition effectiveness at the time of introducing large flow rate material gas is high, by being easy to activate the decomposition effectiveness of the hydrogen under hydrogen extensive dilution highly, etc. increased in order that the decomposition effectiveness of material gas is high, especially the rate of sedimentation by using microwave.

[0075] Moreover, compared with the case where RF plasma-CVD method is used, when forming microcrystal silicon by the microwave plasma-CVD method, since high-speed membrane formation is attained, substrate temperature can also be made high and it is thought that the good microcrystal silicon of membraneous quality was able to be formed.

[0076] Furthermore, it was able to raise lessening the rate of photodegradation, i.e., stabilization conversion efficiency, comparatively, being able to control the thermal damage under middle cell production to the minimum, and maintaining photoelectric conversion efficiency high as a triple cell by having used the hot good microcrystal silicon created by the microwave plasma-CVD method in i type layer of POTOMUSERU, even if it uses microcrystal silicon for the middle cell by this invention as an i type layer.

[0077] Moreover, conveying a band-like substrate continuously, by combining the so-called roll-to-roll process which forms a thin film in a substrate front face, and the above-mentioned microwave plasma-CVD method, the localized level [ / near the interface of two or more semi-conductor layers ] was able to be decreased, and the photoelectric conversion efficiency of a photovoltaic cell was able to be raised.

[0078] Drawing 1 is the schematic diagram showing typically the cross section of the laminating mold photovoltaic cell of this invention. In drawing 1, the laminating mold photovoltaic cell of this invention is having structure where the laminating of the configuration component of three pin junction was carried out on the substrate 120, 150 is counted from an optical incidence side, and, as for the first pin junction and 140, the second pin junction and 130 are the third pin junction.

[0079] A laminating is carried out on the metal layer 101 formed on the base 100, and the transparence conductive layer 102, a transparent electrode 115 and the current collection electrode 116 are formed in the topmost part of three pin junction, and these three pin junction forms the photovoltaic cell of a stack mold.

[0080] And each pin junction consists of n type layer 112, n mold microcrystal semi-conductor layers 103 and 108, i type layers 106 and 113, i mold microcrystal semi-conductor layers 105 and 110, and p type layers 107, 111, and 114.

[0081] Moreover, in this invention, microcrystal silicon is used as an i type layer 105 of the third pin junction, using microcrystal silicon as an i type layer 110 of the second pin junction, using amorphous silicon as an i type layer 113 of the first pin junction.

[0082] Drawing 2 is the schematic diagram showing typically other cross-section structures of the laminating mold photovoltaic cell of this invention. In drawing 2, the laminating mold photovoltaic cell of this invention is having structure where the laminating of the configuration component of three pin junction was carried out on the substrate 220, 250 is counted from an optical incidence side, and, as for the first pin junction and 240, the second pin junction and 230 are the third pin junction.



[0083] A laminating is carried out on the metal layer 201 formed on the base 200, and the transparent conductive layer 202, a transparent electrode 215 and the current collection electrode 216 are formed in the topmost part of three pin junction, and these three pin junction forms the photovoltaic cell of a stack mold.

[0084] And each pin junction consists of n type layers 208 and 212, n mold microcrystal semi-conductor layers 203 and 209, i type layers 206 and 213, i mold microcrystal semi-conductor layers 205 and 210, and p type layers 207, 211, and 214.

[0085] Moreover, in this invention, microcrystal silicon is used as an i type layer 205 of the third pin junction, using microcrystal silicon as an i type layer 210 of the second pin junction, using amorphous silicon as an i type layer 213 of the first pin junction.

[0086] Drawing 3 is the schematic diagram showing typically another cross-section structure of the laminating mold photovoltaic cell of this invention. In drawing 3, the laminating mold photovoltaic cell of this invention is having structure where the laminating of the three pin junction was carried out on the substrate 320, 350 is counted from an optical incidence side, and, as for the first pin junction and 340, the second pin junction and 330 are the third pin junction.

[0087] A laminating is carried out on the metal layer 301 formed on the base 300, and the transparent conductive layer 302, a transparent electrode 315 and the current collection electrode 316 are formed in the topmost part of three pin junction, and these three pin junction forms the photovoltaic cell of a stack mold.

[0088] And each pin junction consists of n type layers 317 and 312, n mold microcrystal semi-conductor layers 303 and 308, i type layers 306 and 313, i mold microcrystal semi-conductor layers 305 and 310, and p type layers 307, 311, and 314.

[0089] Moreover, in this invention, microcrystal silicon is used as an i type layer 305 of the third pin junction, using microcrystal silicon as an i type layer 310 of the second pin junction, using amorphous silicon as an i type layer 313 of the first pin junction.

[0090] In addition, in drawing 1 thru/or the laminating mold photovoltaic cell of drawing 3, the configuration which replaced n type layer and p type layer of pin junction can also be taken.

[0091] Hereafter, each component of the laminating mold photovoltaic cell of this invention is explained in more detail based on drawing 1.

[0092] (Substrate) Since the semi-conductor layers 103-114 are about 5 micrometers [ at most ] thin films, they are deposited on a suitable substrate. As such a substrate 100, you may be the thing of the quality of a single crystal, or the quality of a non-single crystal, and may be a conductive thing, and may be the thing of electric insulation further. Moreover, although these may be the things of translucency or may be the things of non-translucency, there are little deformation and distortion and it is desirable that it is what has desired reinforcement.

[0093] Specifically Fe, nickel, Cr, aluminum, Mo, Au, Nb, Ta, V, Sheet metal or its complex, such as metals, such as Ti, Pt, and Pb, or these alloys, for example, brass, and stainless steel, Or polyester, polyethylene, a polycarbonate, cellulose acetate, Polypropylene, a polyvinyl chloride, a polyvinylidene chloride, polystyrene, The film or sheets of heat-resistant synthetic resin, such as a polyamide, polyimide, and epoxy, Or these, glass fiber, a carbon fiber, a boron fiber, Insulating thin films, such as a metal thin film of the different-species quality of the material or/and SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, aluminum<sub>2</sub>O<sub>3</sub>, and AlN, on front faces, such as complex with a metal fiber etc. or sheet metal of these metals, and a resin sheet, the sputtering method, The thing which performed surface coating processing by vacuum deposition, electroplating, etc. or glass, the ceramics, etc. are mentioned.

[0094] In order to use as a substrate for photovoltaic cells, when band-like substrates are conductors, such as a metal, it is good also as an electrode for direct current ejection, and On the near front face in which the deposition film is formed when it is insulators, such as synthetic resin, aluminum, Ag, Pt, Au, nickel, Ti, Mo, W, Fe, V, Cr, Cu, It is desirable to perform surface treatment for the so-called metal simple substances, such as stainless steel, brass, Nichrome, SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>, and ZnO, ITO, an alloy, or a transparent conductive oxide (TCO) beforehand by approaches; such as plating, vacuum evaporation, and sputtering, and to form the electrode for current ejection.

[0095] of course -- even if band-like substrates are conductors, such as a metal, -- a long wave -- the reflection factor on Nagamitsu's substrate front face may be raised, or a metal layer of a different kind for the purpose of preventing the counter diffusion of the configuration element between the substrate quality of the material and the deposition film etc. may be prepared in the side in which the deposition film on a substrate is formed. Moreover, a substrate is comparatively transparent, and when considering as the photovoltaic cell of the lamination which performs optical incidence from a substrate side, it is desirable to carry out deposition formation of the conductive thin films, such as a transparent conductive oxide metallurgy group thin film, beforehand.

[0096] The front-face nature of a substrate may be the so-called smooth side, or may be a minute concave convex. In considering as a minute concave convex, the shape of the toothing has the shape of the shape of a globular shape and a cone, and a pyramid etc., and by setting the maximum height ( $R_{max}$ ) to 0.05 micrometers thru/or 2 micrometers preferably, the light reflex in this front face turns into scattered reflection, and it brings about increase of the optical path length of the reflected light. An application can constitute the configuration of a substrate in the shape of tabular [ on a smooth front face or the front face of uneven ], and a long belt, and cylindrical \*\*, and although it determines suitably that the thickness can form the photovoltaic cell as a request, when [ as which flexibility is required as a photovoltaic cell ] carried out, or when optical incidence is made from a substrate side, the function as a substrate can make it as thin as possible within limits demonstrated enough.

[0097] However, it may usually be 10 micrometers or more from points, such as a mechanical strength, on manufacture of a substrate, and handling.

[0098] (A rear-face electrode, light reflex layer) The rear-face electrode used for this invention is an electrode arranged on the rear face of a semi-conductor layer to the direction of optical incidence. Therefore, when the location of 101 of drawing 1 or a substrate 100 carries out incidence of the light from the direction of a substrate by translucency, it is arranged in the location of 115.

[0099] As an ingredient of a rear-face electrode, alloys, such as metals, such as gold, silver, copper, aluminum, nickel, iron, chromium, molybdenum, a tungsten, titanium, cobalt, a tantalum, niobium, and a zirconium, or stainless steel, are mentioned.

[0100] Especially, especially a metal with the high reflection factor of aluminum, copper, silver, gold, etc. is desirable. When using a metal with a high reflection factor, it can be made to serve as the role of the light reflex layer which reflects again in a semi-conductor layer the light which was not able to be absorbed in a semi-conductor layer to a rear-face electrode.

[0101] Moreover, although the configuration of a rear-face electrode may be flat, it is more desirable to have the shape of toothing scattered about in light. By having the shape of toothing scattered about in light, the long wavelength light which was not able to be absorbed in a semi-conductor layer is scattered, the optical path length within a semi-conductor layer is carried in a continuation, the long wavelength sensibility of a photovoltaic cell is raised, a short-circuit current can be increased and photoelectric conversion efficiency can be raised. As for the shape of toothing scattered about in light, it is desirable for the difference of a concavo-convex crest and the height of a trough to be 0.2 micrometers to 2.0 micrometers in  $R_{max}$ .

[0102] However, when a substrate serves as a rear-face electrode, formation of a rear-face electrode may not be needed.

[0103] Moreover, vacuum deposition, the sputtering method, plating, print processes, etc. are used for formation of a rear-face electrode. Furthermore, when forming a rear-face electrode in the shape of [ which are scattered about in light ] toothing, it is formed by carrying out dry etching of the film of the formed metal or an alloy, carrying out wet etching, carrying out sandblasting, or heating etc. Moreover, the shape of toothing scattered about in light can also be formed by vapor-depositing an above-mentioned metal or an above-mentioned alloy, heating a substrate.

[0104] Between the rear-face electrode 101 and n mold microcrystal semi-conductor layer 103, the diffusion prevention layers 102, such as a conductive zinc oxide, may be formed. It not only prevents that the metallic element which constitutes the lower electrode 101 is spread into n mold microcrystal semi-conductor layer as effectiveness of a diffusion prevention layer, but The short-circuit generated by

the defect of a pinhole etc. between the rear-face electrodes 101 and transparent electrodes 115 which were prepared on both sides of the semi-conductor layer by giving the resistance of  $1000 \Omega$  is prevented, And effectiveness, such as shutting up the light by which was made to generate the multiplex interference by the thin film, and incidence was carried out in a photovoltaic cell, can be mentioned.

[0105] (i type layer: Intrinsic-semiconductor layer) Especially i type layer used for pin junction in the photovoltaic cell using an IV-IV group and an III-V group alloy system amorphous semiconductor ingredient is an important layer which carries out generating transportation of the carrier to exposure light.

[0106] As an i type layer, the layer of n mold can also be slightly used [ p mold and ] for whether to be small.

[0107] Into an IV-IV group and an III-V group alloy system amorphous semiconductor ingredient, a hydrogen atom (H, D) or a halogen atom (X) contains, and this has important work into them. The hydrogen atom (H, D) or halogen atom (X) contained in i type layer serves to compensate the uncombined hand (dangling bond) of i type layer, and raises the mobility of KIARIA in i type layer, and the product of a life. Moreover, it serves to compensate the interface state density of the field side of p type layer / i type layer, and an n type layer / i type layer, and is effective in raising the photoelectromotive force, the photocurrent, and the optical responsibility of a photovoltaic cell.

[0108] The hydrogen atom or/and halogen atom which are contained in i type layer are mentioned as a content with optimal 1 - 40at%. That over which many contents of a hydrogen atom or/and a halogen atom are especially distributed by the field side side of p type layer / i type layer, and an n type layer / i type layer is mentioned as a desirable distribution gestalt, and the content of the hydrogen atom near [ this ] the interface or/and a halogen atom is mentioned as range where the twice [ 1.05 to ] as many range as the content in bulk is desirable. Furthermore, it is desirable that the content of a hydrogen atom or/and a halogen atom is changing corresponding to the content of a silicon atom.

[0109] In the photovoltaic cell of this invention, amorphous silicon is used as a semiconductor material which constitutes i type layer 113 of the first pin junction 150, microcrystal silicon is used as a semiconductor material which constitutes i type layer 110 of the second pin junction 140 of this invention, and microcrystal silicon is used as a semiconductor material which constitutes i type layer 105 of the third pin junction 130.

[0110] a-Si:H, a-Si:F, a-Si:H:F, muc-Si:H, muc-Si:F, muc-Si:H:F [ amorphous silicon and microcrystal silicon ], etc. are written with the element with which a dangling bond is compensated.

[0111] As an i type layer 113 of the first suitable pin junction 150 for the laminating mold photovoltaic cell of this invention, specifically The hydrogenation amorphous silicon (a-Si:H) of i mold is mentioned. As the property The content (CH) of 1.60eV - 1.90eV and a hydrogen atom 1.0 - 25.0%, [ an optical band gap ( $E_g$ ) ] The optical electric conductivity under the false sunlight exposure of AM1.5 and 100 mW/cm<sup>2</sup> (sigmap) 1.0x10 to 5 or more S/cm, As for 55 or less meVs and localized level density, a three or less 10<sup>17</sup>/cm<sup>3</sup> thing is suitably used for the ABAKKU energy according [ dark electric conductivity (sigmad) ] to 1.0x10 to 9 S/less than cm, and a constant photograph current method (CPM).

[0112] 0.5-micrometer or more range of the thickness of the microcrystal silicon which constitutes i type layer 110 of the second pin junction 140 of the photovoltaic cell of this invention is 1.5 micrometers or less. Moreover, the microcrystal silicon which constitutes i type layer of the second pin junction contains boron, and the boron content is 8 ppm or less. Furthermore, the light absorption multiplier of 950nm of the microcrystal silicon which is i type layer of the second pin junction is one or more [ 200cm<sup>-1</sup> ]. And the microcrystal silicon which is i type layer of the second pin junction is formed by the microwave plasma-CVD method.

[0113] Moreover, 1.5-micrometer or more range of the microcrystal silicone film thickness which constitutes i type layer 105 of the third pin junction 130 of the photovoltaic cell of this invention is 3.5 micrometers or less. Moreover, the microcrystal silicon which is i type layer of the third pin junction contains boron, and the boron content is 8 ppm or less. Furthermore, the light absorption multiplier of 950nm of the microcrystal silicon which is i type layer of the third pin junction is one or more [ 200cm<sup>-1</sup> ]. And the microcrystal silicon which is i type layer of the third pin junction is formed by the microwave

plasma-CVD method.

[0114] (p type layer or n type layer) p type layer or n type layer is also an important layer which influences the property of the laminating mold photoelectromotive-force equipment of this invention.

[0115] As the amorphous ingredient (it is written as "a -") of p type layer or n type layer, and a microcrystal ingredient (it is written as "muc -") For example, a-Si:H, a-Si:HX, a-SiC:H, a-SiC:HX, a-SiGe:H, a-SiGeC:H, a-SiO:H, a-SiN:H, a-SiON:HX, a-SiOCN:HX, muc-Si:H, muc-SiC:H, muc-Si:HX, muc-SiC:HX, muc-SiGe:H, muc-SiO:H, muc-SiGeC:H, muc-SiN:H, muc-SiON:HX, The ingredient which added the valence-electron control agent (the [ periodic table ] III group atom : B, aluminum, Ga, In, Tl) of p mold and the valence-electron control agent (periodic table Vth group atom : P As, Sb, and Bi.) of n mold to high concentration is mentioned to muc-SiOCN:HX etc.

[0116] As a polycrystal ingredient (it is written as "poly -"), the ingredient which added the valence-electron control agent (the [ periodic table ] III group atom : B, aluminum, Ga, In, Tl) of p mold and the valence-electron control agent (periodic table Vth group atom : P As, Sb, and Bi.) of n mold to high concentration is mentioned, for example to poly-Si:H, poly-Si:HX, poly-SiC:H, poly-SiC:HX, poly-SiGe:H, poly-Si, poly-SiC, poly-SiGe, etc.

[0117] Especially, the crystalline semi-conductor layer with little light absorption or the large amorphous semiconductor layer of a band gap is suitable for p type layer or n type layer by the side of optical incidence.

[0118] the [ to p type layer / periodic table ] -- as for the addition of an III group atom, and the addition of the Vth group atom of a periodic table to n type layer, 0.1 - 50at% is mentioned as an optimal amount.

[0119] Moreover, the hydrogen atom (H, D) or halogen atom contained in p type layer or n type layer serves to compensate the uncombined hand of p type layer or n type layer, and raises the doping effectiveness of p type layer or n type layer. As for the hydrogen atom or halogen atom added in p type layer or n type layer, 0.1 - 40at% is mentioned as an optimal amount. Especially, when p type layer or n type layer is crystallinity, as for a hydrogen atom or a halogen atom, 0.1 - 8at% is mentioned as an optimal amount.

[0120] Furthermore, that over which many contents of a hydrogen atom or/and a halogen atom are distributed by the field side side of p type layer / i type layer, and an n type layer / i type layer is mentioned as a desirable distribution gestalt, and the content of the hydrogen atom near [ this ] the interface or/and a halogen atom is mentioned as range where the twice [ 1.05 to ] as many range as the content in bulk is desirable.

[0121] Thus, the defective level near [ this ] the interface and mechanical distortion can be decreased, and the photoelectromotive force and the photocurrent of a laminating mold photovoltaic cell of this invention can be made to increase by making [ many ] the content of a hydrogen atom or a halogen atom near the field side of p type layer / i type layer, and an n type layer / i type layer.

[0122] As an electrical property of p type layer of a photovoltaic cell, or n type layer, a thing 0.2eV or less has desirable activation energy, and a thing 0.1eV or less is the optimal. Moreover, as un-resisting, below 100-ohmcm is desirable, and below 1-ohmcm is the optimal. Furthermore, the thickness of p type layer or n type layer has desirable 1-50nm, and its 3-10nm is the optimal.

[0123] (The formation approach of a semi-conductor layer) The manufacture approach most suitable in order to form suitable IV group and an III-V group alloy system amorphous semiconductor layer as a semi-conductor layer of the laminating mold photoelectromotive-force equipment of this invention is a microwave plasma-CVD method, and the suitable manufacture approach for a degree is RF plasma-CVD method.

[0124] A microwave plasma-CVD method introducing ingredient gas, such as material gas and dilution gas, into the deposition room (vacuum chamber) which changes into a reduced pressure condition, and exhausting with a vacuum pump Fix internal pressure of a deposition room and the microwave oscillated by the microwave power source is drawn with a waveguide or a coaxial cable. It introduces into a deposition room through dielectric windows (alumina ceramics etc.) or the conductor (rods, such as nickel, W, and stainless steel) electrically insulated from the deposition room. The plasma of ingredient

gas is made to occur and it decomposes, and on the substrate arranged in the deposition interior of a room, it is the approach of forming the desired deposition film, and the deposition film applicable to a photovoltaic cell can be formed on large deposition conditions.

[0125] When depositing the semi-conductor layer of the laminating mold photovoltaic cell of this invention by the microwave plasma-CVD method, 250-500 degrees C of substrate temperature of the deposition interior of a room are mentioned, and 0.5 - 250mTorr and microwave power are mentioned for internal pressure as range where the frequency of 3 and microwave has desirable 0.1-10GHz 0.01-1 W/cm.

[0126] Moreover, when depositing by RF plasma-CVD method, 100-350 degrees C of substrate temperature of the deposition interior of a room are mentioned, and 0.1 - 10torr and RF power are mentioned for internal pressure as conditions with 0.1 - 15 A/sec suitable for 0.01 - 5.0 W/cm<sup>2</sup> and the rate of sedimentation.

[0127] Moreover, there are some which are depended on a roll two roll (Roll-to-Roll) method as the deposition film formation approach of having been suitable for formation of the semi-conductor layer of the laminating mold photovoltaic cell of this invention. This deposition film formation approach is arranged in accordance with the path which carries out sequential penetration of two or more glow discharge fields, carrying out deposition formation of the semi-conductor layer of the conductivity type needed in each glow discharge field, can make that longitudinal direction able to convey a band-like substrate continuously, and can form continuously the photovoltaic cell which has desired semi-conductor junction by this.

[0128] As material gas suitable for deposition of the suitable IVIV group for the laminating mold photoelectromotive-force equipment of this invention, and an III-V group alloy system amorphous semiconductor layer, the mixed gas of these compounds, such as the compound containing a silicon atom which can be gasified, the compound containing a germanium atom which can be gasified, the compound containing a carbon atom which can gasify, the compound containing a nitrogen atom which can gasify, and the compound containing an oxygen atom which can gasify, can mention.

[0129] As a compound containing a silicon atom which can be gasified For example, SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub>, SiF<sub>4</sub> and SiFH<sub>3</sub>, SiF<sub>2</sub>H<sub>2</sub>, SiF<sub>3</sub>H, the shape of a chain and an annular silane compound are used. Si<sub>3</sub>H<sub>8</sub>, SiD<sub>4</sub> and SiHD<sub>3</sub>, SiH<sub>2</sub>D<sub>2</sub>, SiH<sub>3</sub>D, SiFD<sub>3</sub>, SiF<sub>2</sub>D<sub>2</sub>, Si<sub>2</sub>D<sub>3</sub>H<sub>3</sub>, 5, (SiF<sub>2</sub>)<sub>6</sub>, (SiF<sub>2</sub>)<sub>4</sub>, Si<sub>2</sub>F<sub>6</sub>, Si<sub>3</sub>F<sub>8</sub>, Si<sub>2</sub>H<sub>2</sub>F<sub>4</sub>, Si<sub>2</sub>H<sub>3</sub>F<sub>3</sub>, SiCl<sub>4</sub> and 5 (SiCl<sub>2</sub>), SiBr<sub>4</sub> and 5 (SiBr<sub>2</sub>), and Si<sub>2</sub> -- the thing of gas conditions, such as Cl<sub>6</sub>, SiHCl<sub>3</sub>, SiH<sub>2</sub>B<sub>r</sub><sub>2</sub>, SiH<sub>2</sub>Cl<sub>2</sub>, and Si<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>, -- Or what can be gasified easily is mentioned.

[0130] As a compound containing a germanium atom which can be gasified, GeH<sub>4</sub>, GeD<sub>4</sub>, GeF<sub>4</sub>, GeFH<sub>3</sub>, GeF<sub>2</sub>H<sub>2</sub>, GeF<sub>3</sub>H, GeHD<sub>3</sub>, GeH<sub>2</sub>D<sub>2</sub>, GeH<sub>3</sub>D, germanium<sub>2</sub>H<sub>6</sub>, germanium<sub>2</sub>D<sub>6</sub>, etc. are mentioned.

[0131] As a compound containing a carbon atom which can be gasified, CH<sub>4</sub>, CD<sub>4</sub>, C<sub>n</sub>H<sub>2n+2</sub> (n is an integer), C<sub>n</sub>H<sub>2n</sub> (n is an integer), C<sub>2</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, CO<sub>2</sub>, CO, etc. are mentioned.

[0132] As nitrogen content gas, N<sub>2</sub>, NH<sub>3</sub>, ND<sub>3</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O, etc. are mentioned.

[0133] As oxygen content gas, O<sub>2</sub>, CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>OH, etc. are mentioned.

[0134] moreover -- as the matter introduced into p type layer or n type layer in order to carry out valence-electron control -- the [ periodic table ] -- an III group atom and the Vth group atom are mentioned.

[0135] the -- as what is effectively used as starting material for III group atom installation As an object for boron atom installation, for example, hydrogenation boron, such as B-2 H<sub>6</sub>, B<sub>4</sub> H<sub>10</sub>, B<sub>5</sub> H<sub>9</sub>, B<sub>5</sub> H<sub>11</sub>, B<sub>6</sub> H<sub>10</sub>, B<sub>6</sub> H<sub>12</sub>, and B<sub>6</sub> H<sub>14</sub>, The halogenation boron of BF<sub>3</sub> and BCl<sub>3</sub> grade etc. can be mentioned, in addition AlCl<sub>3</sub>, GaCl<sub>3</sub>, InCl<sub>3</sub>, TlCl<sub>3</sub>, etc. can be mentioned, and especially B-2s H<sub>6</sub> and BF<sub>3</sub> are suitable.

[0136] Being effectively used as starting material for the Vth group atom installation As an object for phosphorus atom installation, for example, hydrogenation phosphorus, such as PH<sub>3</sub> and P<sub>2</sub>H<sub>4</sub>, PH<sub>4</sub>I, Halogenation phosphorus, such as PF<sub>3</sub>, PF<sub>5</sub>, and PCl<sub>3</sub>, PCl<sub>5</sub>, PBr<sub>3</sub>, PBr<sub>5</sub>, PI<sub>3</sub>, is mentioned. In addition, AsH<sub>3</sub>, AsF<sub>3</sub>, AsCl<sub>3</sub>, AsBr<sub>3</sub>, AsF<sub>5</sub>, SbH<sub>3</sub>, SbF<sub>3</sub>, SbF<sub>5</sub>, SbCl<sub>3</sub>, SbCl<sub>5</sub>, BiH<sub>3</sub>, BiCl<sub>3</sub>, BiBr<sub>3</sub>,

etc. can be mentioned, and especially PH<sub>3</sub> and PF<sub>3</sub> are suitable.

[0137] Moreover, the compound which the above can gasify may be suitably diluted with gas, such as H<sub>2</sub>, helium, Ne, Ar, Xe, and Kr, and you may introduce into a deposition room.

[0138] Especially when [ that are light absorption, such as a microcrystal semi-conductor and a-SiC:H, ] it is few or deposits the large layer of band GIAPU, it is desirable to dilute material gas with hydrogen gas 2 to 100 times, and to introduce microwave power or RF power by comparatively high power.

[0139] (Transparent electrode) In this invention, a transparent electrode 115 serves also as a role of an antireflection film by optimizing the thickness while being an electrode by the side of the optical incidence which penetrates light. It is required for a transparent electrode 115 that it has high permeability in the wavelength field which can absorb a semi-conductor layer, and that resistivity should be low. Preferably, it is desirable for the permeability in 550nm to be 85% or more more preferably 80% or more.

[0140] Moreover, as for the resistivity of a transparent electrode, it is preferably desirable that it is below  $1 \times 10^{-3}$  ohmcm more preferably below  $5 \times 10^{-3}$  ohmcm.

[0141] As an ingredient of a transparent electrode, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, ITO (In<sub>2</sub>O<sub>3</sub>+SnO<sub>2</sub>), ZnO and CdO, Cd<sub>2</sub>SnO<sub>4</sub>, TiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>, Bi<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, the conductive oxide of Na<sub>x</sub>WO<sub>3</sub> grade, or the thing that mixed these is used suitably.

[0142] Moreover, the element (dopant) from which conductivity is changed to these compounds may be added. the case where a transparent electrode 103 is ZnO as an element (dopant) to which conductivity is changed, for example -- aluminum, In, B, Ga, Si, F, etc. -- moreover, in In<sub>2</sub>O<sub>3</sub>, Sn, F, Te, Ti, Sb, Pb, etc. are used, and, in SnO<sub>2</sub>, F, Sb, P, As, In, Ti, Te, W, Cl, Br, I, etc. are used further suitably.

[0143] Moreover, as the formation approach of a transparent electrode, vacuum deposition, a CVD method, a spray method, the spin turning-on method, a dip method, etc. are used suitably.

[0144] (Current collection electrode) In this invention, the current collection electrode 116 serves to form in the part on a transparent electrode 115 if needed, when the resistivity of a transparent electrode 115 is not made sufficiently low, to lower the resistivity of an electrode, and to lower the series resistance of a photovoltaic cell.

[0145] Conductive paste using alloys, such as metals, such as gold, silver, copper, aluminum, nickel, iron, chromium, molybdenum, a tungsten, titanium, cobalt, a tantalum, niobium, and a zirconium, or stainless steel, or a powdered metal as an ingredient of a current collection electrode etc. is mentioned. And the configuration is formed in a pectinate form so that the incident light to a semi-conductor layer may not be interrupted as much as possible.

[0146] Moreover, it is more preferably desirable [ the area which a current collection electrode occupies in the area of the whole photovoltaic cell ] the optimal [ 5% or less of ] 10% or less 15% or less preferably.

[0147] As the formation approach, vacuum deposition, the sputtering method, plating, print processes, etc. are used for formation of the pattern of a current collection electrode using a mask.

[0148] In addition, when manufacturing desired output voltage and the photoelectromotive-force equipment of the output current using the laminating mold photovoltaic cell of this invention, the laminating mold photovoltaic cell of this invention is connected to a serial or juxtaposition, a protective layer is formed in a front face and a rear face, and the ejection electrode of an output etc. is attached. Moreover, when carrying out series connection of the laminating mold photovoltaic cell of this invention, the diode for antisuckbacks may be incorporated.

[0149]

[Example] Although the suitable example of this invention is explained below, this invention is not limited to these examples at all.

[0150] <<example 1>> The laminating mold photovoltaic cell shown in drawing 1 was produced using the deposition equipment shown in drawing 4. deposition equipment 400 -- MWPCVD -- law and RFPCVD -- the both sides of law can be carried out. Each semi-conductor layer was formed on the substrate 490 which has the light reflex layers 101 and 102 using this deposition equipment 400.

[0151] a non-illustrated raw material chemical cylinder is connected to deposition equipment through

gas installation tubing, and it is [ come out and ]. Each raw material chemical cylinder was refined by the super-high grade, and connected SiH<sub>4</sub> chemical cylinder, CH<sub>4</sub> chemical cylinder, GeH<sub>4</sub> chemical cylinder, Si<sub>2</sub>H<sub>6</sub> chemical cylinder, PH<sub>3</sub>/H<sub>2</sub> (dilution: 2.0%) chemical cylinder, B-2H<sub>6</sub>-/H<sub>2</sub> (dilution: 2.0%) chemical cylinder, H<sub>2</sub> chemical cylinder, helium chemical cylinder, SiCl<sub>2</sub>H<sub>2</sub> gas POMBE, and SiH<sub>4</sub>/H<sub>2</sub> (dilution: 2.0%) chemical cylinder.

[0152] Next, the substrate 490 with which the metal layer 101 and the transperence conductive layer 102 are formed has been arranged on the rail 413 for substrate conveyance in the load chamber 401, and evacuation was carried out until the pressure was set to abbreviation 1x10<sup>-5</sup>Torr on the non-illustrated evacuation pump in the inside of the \*\* reloading chamber 401.

[0153] Furthermore, the conveyance chamber 402 which carried out vacuum suction beforehand with the non-illustrated evacuation pump, and the HEGETO bulb 406 in the deposition chamber 417 were opened and conveyed. The rear face of a substrate 490 was stuck at the heater 410 for substrate heating, and it heated, and evacuation was carried out until the pressure was set to abbreviation 1x10<sup>-5</sup>Torr by evacuation BOMPU whose inside of the deposition chamber 417 is not illustrated.

[0154] After preparation of membrane formation was completed as mentioned above, H<sub>2</sub> gas was introduced through the gas installation tubing 429 in the deposition chamber 417, bulbs 441, 431, and 430 were opened so that H<sub>2</sub> quantity of gas flow might be set to 300sccm(s), and the massflow controller 436 adjusted. The non-illustrated conductance bulb adjusted so that the pressure in the deposition chamber 417 might be set to 1.0Torr(s). The heater 410 for substrate heating was set up so that the temperature of a substrate 490 might become 350 degrees C, and the 3rd RFn type layer 103 which consists of muc-Si was formed in the place by which substrate temperature was stabilized.

[0155] In order to have formed the 3rd RFn type layer 103 which consists of muc-Si, in the deposition chamber 417, bulbs 443, 433, 444, and 434 were operated and SiH<sub>4</sub> gas and PH<sub>3</sub>/H<sub>2</sub> gas were introduced through the gas installation tubing 429.

[0156] At this time, the flow rate of SiH<sub>4</sub> gas adjusted with massflow controllers 438, 436, and 439 so that the flow rate of 90sccm(s) and PH<sub>3</sub>/H<sub>2</sub> gas might serve as [ the flow rate of 0.4sccm(s) and H<sub>2</sub> gas ] 0.5sccm(s), and it adjusted the pressure in the deposition chamber 417 so that it might be set to 1.0Torr (s).

[0157] Set the power of the RF (it is written as "RF" below.) power source 422 as 0.55 W/cm<sup>3</sup>, introduced RF power into the cup 420 for plasma formation, glow discharge was made to occur, RF power source was shut off in the place which started formation of the 3rd RFn type layer and formed the 3rd RFn type layer of 10nm of thickness on the substrate, and formation of a stop and the 3rd RFn type layer 103 was finished for glow discharge. Evacuation of a stop, the deposition interior of a room, and the inside of gas piping was carried out for the inflow of SiH<sub>4</sub> gas into the deposition chamber 417, PH<sub>3</sub>/H<sub>2</sub> gas, and H<sub>2</sub> gas to 1x10<sup>-5</sup>Torr.

[0158] Next, sequential formation of the 3rd MWi type layer 105 which consists of muc-Si, and the 3rd RFi type layer 106 which consists of a-Si was carried out.

[0159] First, the vacuum suction RE \*\*\*\*\* conveyance chamber 403 and the HEGETO bulb 407 in i type layer deposition chamber 418 were beforehand opened with the non-illustrated evacuation pump, and the substrate 490 was conveyed. The rear face of a substrate 490 was stuck at the heater 411 for substrate heating, and it heated, and evacuation was carried out until the pressure was set to abbreviation 1x10<sup>-5</sup>Torr with the evacuation pump whose inside of i type layer deposition chamber 418 is not illustrated.

[0160] In order to produce the 3rd MWi type layer which consists of muc-Si, the heater 411 for substrate heating was set up so that the temperature of a substrate 490 might become 300 degrees C, bulbs 461, 451, 450, 463, and 453 were opened gradually in the place where the substrate was heated enough, and SiH<sub>4</sub> gas and H<sub>2</sub> gas were made to flow in i type layer deposition chamber 418 through the gas installation tubing 449.

[0161] At this time, the flow rate of SiH<sub>4</sub> gas adjusted with each massflow controllers 456 and 458 so that the flow rate of 80sccm(s) and H<sub>2</sub> gas might serve as 2400sccm(s). The pressure in i type layer deposition chamber 418 adjusted opening of a non-illustrated conductance bulb so that it might be set to



50mTorr. The RF power source 424 was set as 0.22 W/cm<sup>3</sup>, and it was impressed by the bias rod 428. [0162] Then, the power of a non-illustrated microwave power source (2.45GHz) is set as 0.12 W/cm<sup>3</sup>. Introduce muW power in i type layer deposition chamber 418 through a waveguide 426 and the aperture 425 for microwave installation, and glow discharge is made to occur. Production of the 3rd MWi type layer was started on the 3rd RFn type layer by opening a shutter 427, the output of a stop and bias power supply 424 was cut for muW glow discharge in the place which produced i type layer of 3.0 micrometers of thickness, and production of the 3rd MWi type layer 105 was finished.

[0163] Bulbs 451 and 453 were closed and evacuation of the inside of a stop, i type layer deposition chamber 418, and gas piping was carried out for the inflow of SiH<sub>4</sub> gas into i type layer deposition chamber 418, and H<sub>2</sub> gas to 1x10<sup>-5</sup>Torr.

[0164] In order to produce the 3rd RFi type layer 106, the heater 411 for substrate heating was set up so that the temperature of a substrate 490 might become 300 degrees C, bulbs 464, 454, 450, 463, and 453 were opened gradually in the place where the substrate was heated enough, and Si<sub>2</sub>H<sub>6</sub> gas and H<sub>2</sub> gas were made to flow in i type layer deposition chamber 418 through the gas installation tubing 449.

[0165] At this time, the flow rate of Si<sub>2</sub>H<sub>6</sub> gas adjusted with each massflow controllers 459 and 458 so that the flow rate of 3.8sccm(s) and H<sub>2</sub> gas might serve as 100sccm(s). The pressure in i type layer deposition chamber 418 adjusted opening of a non-illustrated conductance bulb so that it might be set to 0.8Torr.

[0166] Next, set the RF power source 424 as 0.0088 W/cm<sup>3</sup>, and it was impressed by the bias rod 428, glow discharge was made to occur, production of the 3rd RFi type layer was started on the 3rd MWi type layer by opening a shutter 427, the output of a stop and the RF power source 424 was cut for RF glow discharge in the place which produced i type layer of 23nm of thickness, and production of the 3rd RFi type layer 106 was finished.

[0167] Bulbs 464, 454, 453, and 450 were closed and evacuation of the inside of a stop, i type layer deposition chamber 418, and gas piping was carried out for the inflow of Si<sub>2</sub>H<sub>6</sub> gas into i type layer deposition chamber 418, and H<sub>2</sub> gas to 1x10<sup>-5</sup>Torr.

[0168] Next, in order to have formed the 3rd RFp type layer 107 which consists of SiC, the conveyance chamber 404 which carried out vacuum suction beforehand with the non-illustrated evacuation pump, and the HEGETO bulb 408 in p type layer deposition chamber 419 were opened, and the substrate 490 was conveyed. The rear face of a substrate 490 was stuck at the heater 412 for substrate heating, and it heated, and evacuation was carried out until the pressure was set to abbreviation 1x10<sup>-5</sup>Torr with the evacuation pump whose inside of p type layer deposition chamber 419 is not illustrated.

[0169] The heater 412 for substrate heating was set up so that the temperature of a substrate 490 might become 300 degrees C, in the deposition chamber 419, bulbs 481, 471, 470, 482, 472, 483, 473, 484, and 474 were operated, and H<sub>2</sub> gas, SiH<sub>4</sub>/H<sub>2</sub> gas, B-2H<sub>6</sub>/H<sub>2</sub> gas, and CH<sub>4</sub> gas were introduced through the gas installation tubing 469 in the place by which substrate temperature was stabilized.

[0170] at this time, the flow rate of 9sccm(s) and CH<sub>4</sub> gas serves as [ the flow rate of H<sub>2</sub> gas / the flow rate of 75sccm(s) and SiH<sub>4</sub>/H<sub>2</sub> gas / the flow rate of 3sccm(s) and B-2H<sub>6</sub>/H<sub>2</sub> gas ] 0.1sccm(s) -- as -- massflow controllers 476, 477, 478, and 479 -- it came out and adjusted. The pressure in the deposition chamber 419 adjusted opening of a non-illustrated conductance bulb so that it might be set to 1.8Torr.

[0171] Set the power of the RF power source 423 as 0.09 W/cm<sup>3</sup>, and introduced RF power into the cup 421 for plasma formation, glow discharge was made to occur, RF power source was shut off in the place which started formation of the 3rd RFp type layer and formed the RFp type layer of thickness 10nm on i type layer, and formation of a stop and the 3rd RFp type layer 107 was finished for glow discharge.

[0172] Bulbs 472, 482, 473, 483, 474, 484, 471, 481, and 470 were closed, and evacuation of the inside of a stop, p type layer deposition chamber 419, and gas piping was carried out for the inflow of SiH<sub>4</sub>/H<sub>2</sub> gas into p type layer deposition chamber 419, B-2H<sub>6</sub>/H<sub>2</sub> gas, CH<sub>4</sub> gas, and H<sub>2</sub> gas to 1x10<sup>-5</sup>Torr.

[0173] Formation of the 2nd RFn type layer 109 which consists of muc-Si first opened the conveyance chamber 403 which carried out vacuum suction beforehand by non-illustrated evacuation BOMPU, and the HEGETO bulb 408 in i type layer deposition chamber 418, conveyed the substrate 490, opened the conveyance chamber 402 which carried out vacuum suction beforehand with the non-illustrated

evacuation pump further, and the HEGETO bulb 407 in n type layer deposition chamber 417, and conveyed the substrate 490.

[0174] The rear face of a substrate 490 was stuck at the heater 410 for substrate heating, and it heated, and evacuation was carried out until the pressure was set to abbreviation  $1 \times 10^{-5}$  Torr with the evacuation pump whose inside of n type layer deposition chamber 417 is not illustrated. The heater 410 for substrate heating was set up so that the temperature of a substrate 490 might become 320 degrees C, in the deposition chamber 417, bulbs 443, 433, 444, and 434 were operated and SiH<sub>4</sub> gas and PH<sub>3</sub>/H<sub>2</sub> gas were introduced through the gas installation tubing 429 in the place by which substrate temperature was stabilized.

[0175] At this time, the flow rate of SiH<sub>4</sub> gas adjusted with massflow controllers 438, 436, and 439 so that the flow rate of 150sccm(s) and PH<sub>3</sub>/H<sub>2</sub> gas might serve as [ the flow rate of 0.6sccm(s) and H<sub>2</sub> gas ] 3sccm(s), and it adjusted the pressure in the deposition chamber 417 so that it might be set to 1.2Torr(s).

[0176] Set the power of the RF power source 422 as 0.07 W/cm<sup>3</sup>, and introduced RF power into the cup 420 for plasma formation, glow discharge was made to occur, RF power source was shut off in the place which started formation of the 2nd RFn type layer and formed the 2nd RFn type layer of 100nm of thickness on the substrate, and formation of a stop and the 2nd RFn type layer 108 was finished for glow discharge.

[0177] Evacuation of a stop, the deposition interior of a room, and the inside of gas piping was carried out for the inflow of SiH<sub>4</sub> gas into the deposition chamber 417, PH<sub>3</sub>/H<sub>2</sub> gas, and H<sub>2</sub> gas to  $1 \times 10^{-5}$  Torr.

[0178] In order to have formed 2nd i type layer 110 which consists of muc-Si, the conveyance chamber 403 which carried out vacuum suction beforehand with the non-illustrated evacuation pump, and the HEGETO bulb 408 in i type layer deposition chamber 418 were opened first, the substrate 490 was conveyed, the conveyance chamber 402 which carried out vacuum suction beforehand with the non-illustrated evacuation pump further, and the HEGETO bulb 407 in n type layer deposition chamber 417 were opened, and the substrate 490 was conveyed.

[0179] The heater 411 for substrate heating was set up so that the temperature of a substrate 490 might become 290 degrees C, bulbs 461, 451, 450, 463, and 453 were opened gradually in the place where the substrate was heated enough, and SiH<sub>4</sub> gas and H<sub>2</sub> gas were made to flow in i type layer deposition chamber 418 through the gas installation tubing 449.

[0180] At this time, the flow rate of SiH<sub>4</sub> gas adjusted with each massflow controllers 456 and 458 so that the flow rate of 45sccm(s) and H<sub>2</sub> gas might serve as 1500sccm(s). The pressure in i type layer deposition chamber 418 adjusted opening of a non-illustrated conductance bulb so that it might be set to 0.04Torr.

[0181] Next, 0.15W /of RF power sources 424 was set as 3 cm, and it was impressed by the bias rod 428. Then, the power of a non-illustrated microwave power source (0.5GHz) is set as 0.10 W/cm<sup>3</sup>. Carry out microwave power installation into i type layer deposition chamber 418 through the bias rod 428, and glow discharge is made to occur. Production of 2nd i type layer was started on the 2nd RFn type layer, the output of a stop and bias power supply 424 was cut for glow discharge in the place arrived at at 0.8 micrometers of thickness, and production of 2nd i type layer 110 was finished.

[0182] Bulbs 451 and 453 were closed and evacuation of the inside of a stop, i type layer deposition chamber 418, and gas piping was carried out for the inflow of SiH<sub>4</sub> gas into i type layer deposition chamber 418, and H<sub>2</sub> gas to  $1 \times 10^{-5}$  Torr.

[0183] After formation of the 2nd RFp type layer 111 which consists of SiC conveyed by the same approach as production of the 3rd RFp type layer 107, the flow rate of 80sccm(s) and SiH<sub>4</sub>/H<sub>2</sub> gas adjusted it with the massflow controller so that the flow rate of 9sccm(s) and CH<sub>4</sub> gas might serve as [ the flow rate of 3sccm(s) and B-2H<sub>6</sub>-/H<sub>2</sub> gas ] 0.2sccm(s), and the flow rate of H<sub>2</sub> gas performed it at the substrate temperature of 260 degrees C. Others were produced like the 3rd RFp type layer.

[0184] Formation of the 1st RFn type layer 112 which consists of a-Si first opened the conveyance chamber 403 which carried out vacuum suction beforehand with the non-illustrated evacuation pump, and the HEGETO bulb 408 in i type layer deposition chamber 418, conveyed the substrate 490, opened

the conveyance chamber 402 which carried out vacuum suction beforehand with the non-illustrated evacuation pump further, and the HEGETO bulb 407 in n type layer deposition chamber 417, and conveyed the substrate 490.

[0185] The flow rate of SiH<sub>4</sub> gas adjusted with massflow controllers 438, 436, and 439 so that the flow rate of 45sccm(s) and PH<sub>3</sub>/H<sub>2</sub> gas might serve as [ the flow rate of 1.1sccm(s) and H<sub>2</sub> gas ] 9sccm(s), and the non-illustrated conductance bulb adjusted so that the pressure in the deposition chamber 417 might be set to 1.05Torr(s). The heater 410 for substrate heating was set up so that the temperature of a substrate 490 might become 230 degrees C, and the 3rd RFn type layer 103 which consists of a-Si was formed in the place by which substrate temperature was stabilized.

[0186] The flow rate of the substrate temperature of 195 degrees C after formation of the 1st RFi type layer 113 which consists of a-Si conveys by the same approach as production of the 3rd RFi type layer 104, and Si<sub>2</sub>H<sub>6</sub> gas adjusted with massflow controllers 464 and 463 so that the flow rate of 2sccm(s) and H<sub>2</sub> gas might serve as 200sccm(s), and it adjusted the pressure in the deposition chamber 417 so that it might be set to 0.75Torr(s). The RFi type layer of 0.1 micrometers of thickness was produced by RF power 0.007 W/cm<sup>3</sup>.

[0187] After formation of the 1st RFp type layer 114 which consists of SiC conveyed by the same approach as production of the 3rd RFp type layer 107, the flow rate of 90sccm(s) and SiH<sub>4</sub>/H<sub>2</sub> gas adjusted it with the massflow controller so that the flow rate of 8sccm(s) and CH<sub>4</sub> gas might serve as [ the flow rate of 3sccm(s) and B-2H<sub>6</sub>-/H<sub>2</sub> gas ] 0.4sccm(s), and the flow rate of H<sub>2</sub> gas performed it at the substrate temperature of 170 degrees C. Others were produced like the 3rd RFp type layer.

[0188] Next, the HEGETO bulb 409 in the unload chamber 405 which carried out vacuum suction beforehand by non-illustrated evacuation BOMPU was opened, the substrate 490 was conveyed, the non-illustrated leak bulb was opened, and the unload chamber 405 was leaked.

[0189] Next, vacuum deposition of the ITO of 70nm of thickness was carried out with the vacuum deposition method as a transparence conductive layer 115 on the 1st RFp type layer 114.

[0190] Next, the mask which the hole of a tandem type opened was carried on the transparence conductive layer 115, and vacuum deposition of the current collection electrode 116 of Kushigata which consists of Cr(40nm)/Ag(1000nm)/Cr (40nm) was carried out with the vacuum deposition method.

[0191] Thus, production of a laminating mold photovoltaic cell was finished. Suppose that this photovoltaic cell is called the SC fruit 1.

[0192] <Example 1 of a comparison> In the example 1, RF was used for muc-Si and 2nd i type layer for a-Si in 3rd n type layer in a-SiGe and 2nd n type layer at a-Si and 3rd i type layer, respectively, and the laminating mold photovoltaic cell was produced. Suppose that this photovoltaic cell is called the SC ratio 1. Production of p type layers other than the above, i type layer, and n type layer was performed like the example 1. Table 11 shows a quantity of gas flow.

[0193]

[Table 11]

(比1)	SiH <sub>4</sub> 流量 sccm	Si <sub>2</sub> H <sub>6</sub> 流量 sccm	CH <sub>4</sub> 流量 sccm	GeH <sub>4</sub> 流量 sccm	H <sub>2</sub> 流量 sccm	PH <sub>3</sub> /H <sub>2</sub> 流量 sccm	B <sub>2</sub> H <sub>6</sub> /H <sub>2</sub> 流量 sccm	SiH <sub>4</sub> /H <sub>2</sub> 流量 sccm	压力 Torr	MW 電力 W/cm <sup>2</sup>	RF 電力 W/cm <sup>2</sup>	基板 温度 °C	層厚 nm
RF n型層	2.2				80	10			1.3		0.05	380	10
RF i型層		3.5			100				0.65		0.008	300	10
MW i型層	48			51	170				0.01	0.1	0.32	380	170
RF i型層		3.5			100				0.65		0.008	300	23
RF p型層			0.1		80		9	3	1.8		0.07	300	10
RF n型層	0.5				100	8			1.2		0.1	320	10
MW i型層	80				250				0.02	0.1	0.205	320	350
RF p型層			0.2		80		9	3	1.7		0.07	260	10
RF n型層	1.1				50	10			1.05		0.04	230	10
RF i型層		2.0			200				0.8		0.007	190	90
RF p型層			0.4		90		8	3	1.6		0.07	170	10

[0194] The decrement of the effectiveness when producing the SC fruit 1 and five SC ratios 1 at a time, respectively, and putting under AM1.5 (100 mW/cm<sup>2</sup>) light exposure at 45 degrees C to initial effectiveness for 3000 hours (It is hereafter written as "the rate of photodegradation".) Effectiveness after setting for 2100 hours to the dark place of the photoelectric conversion efficiency after stabilization (stabilization conversion efficiency), the temperature of 85 degrees C, and 85% of humidity (it is hereafter written as "the rate of heat-resistant degradation".) And it measured about cel withstand voltage and the yield.

[0195] Measurement of initial conversion efficiency and the photoelectric conversion efficiency after stabilization installs the produced photovoltaic cell in the bottom of the optical exposure of AM1.5 (100 mW/cm<sup>2</sup>), and is obtained by measuring a V-I property. The property of the SC ratio 1 came to be shown in Table 1 to the SC fruit 1 as a result of measurement.

[0196]

[Table 1]

試料No	安定化変換効率	光劣化率	耐熱劣化率	セル耐電圧	歩留り
SC 実1	1	1	1	1	1
SC 比1	0.9	1.18	1.14	0.99	0.98

[0197] As mentioned above, it turned out that the laminating mold photovoltaic cell (SC fruit 1) of this invention is superior to the conventional laminating mold photovoltaic cell (SC ratio 1) in stabilization conversion efficiency, the rate of photodegradation, the rate of heat-resistant degradation, cel withstand voltage, and the yield.

[0198] <<example 2>> The frequency of microwave was changed into 0.1GHz, the 3rd i layer 105 which consists of muc-Si in an example 1 was formed, and the same photovoltaic cell was produced.

[0199] The heater 411 for substrate heating was set up so that the temperature of a substrate 490 might become 330 degrees C, bulbs 461, 451, 450, 463, and 453 were opened gradually in the place where the substrate 490 was heated enough, and SiH<sub>4</sub> gas and H<sub>2</sub> gas were made to flow in i type layer deposition chamber 418 through the gas installation tubing 449.

[0200] At this time, the flow rate of SiH<sub>4</sub> gas adjusted with each massflow controllers 456 and 458 so that the flow rate of 60sccm(s) and H<sub>2</sub> gas might serve as 2400sccm(s). The pressure in i type layer deposition chamber 418 adjusted opening of a non-illustrated conductance bulb so that it might be set to 0.2Torr.

[0201] Next, set the power of a non-illustrated microwave power source (0.1GHz) as 0.15 W/cm<sup>3</sup>, and it was impressed by the bias rod 428, glow discharge was made to occur, production of 3rd i type layer was started on the 3rd RFn type layer, and production of a stop and 3rd i type layer 105 was finished for glow discharge in the place which produced i type layer of 2.5 micrometers of thickness.

[0202] Bulbs 451 and 453 were closed and evacuation of the inside of a stop, i type layer deposition chamber 418, and gas piping was carried out for the inflow of SiH<sub>4</sub> gas into i type layer deposition chamber 418, and H<sub>2</sub> gas to 1x10<sup>-5</sup>Torr. Suppose that this laminating mold photovoltaic cell is called the SC fruit 2.

[0203] <Example 2 of a comparison> RF was used for a-Si and 2nd i type layer for a-siGe in 3rd n type layer in an example 1 in a-SiGe and 2nd n type layer at a-Si and 3rd i type layer, respectively, and the laminating mold photovoltaic cell was produced. Suppose that this photovoltaic cell is called the SC ratio 2. Production of p type layers other than the above, i type layer, and n type layer was performed like the example 1. Table 21 shows a quantity of gas flow.

[0204]

[Table 21]

(比2)	SiH <sub>4</sub> 流量 sccm	Si <sub>2</sub> H <sub>6</sub> 流量 sccm	CH <sub>4</sub> 流量 sccm	GeH <sub>4</sub> 流量 sccm	H <sub>2</sub> 流量 sccm	PH <sub>3</sub> /H <sub>2</sub> 流量 sccm	B <sub>2</sub> H <sub>6</sub> /H <sub>2</sub> 流量 sccm	SiH <sub>4</sub> /H <sub>2</sub> 流量 sccm	圧力 Torr	MW 電力 W/cm <sup>2</sup>	RF 電力 W/cm <sup>2</sup>	基板 温度 ℃	層厚 nm
RF n型層	2.2				80	10			1.3		0.05	370	10
RF i型層		3.5			90				0.65		0.008	300	10
MW i型層	48			53	170				0.02	0.1	0.32	370	170
RF i型層		3.5			90				0.67		0.008	300	20
RF p型層			0.1		80		8	3	1.8		0.07	300	10
RF n型層	2.0				70	8			1.2		0.07	320	10
MW i型層	50			35	250				0.02	0.1	0.205	320	140
RF p型層			0.2		80		8	3	1.8		0.07	250	10
RF n型層	1.3				50	10			1.05		0.04	230	10
RF i型層		2.0			100				0.8		0.007	180	90
RF p型層			0.4		90		8	3	1.6		0.07	170	10

[0205] It produced the SC fruit 2 and four SC ratios 2 at a time, respectively, they performed measurement of the photoelectric conversion efficiency after stabilization (stabilization conversion efficiency), the rate of photodegradation, the rate of heat-resistant degradation, cel withstand voltage, and the yield, and computed each average.

[0206] The property of the SC ratio 2 came to be shown in Table 2 to the SC fruit 2 as a result of measurement.

[0207]

[Table 2]

試料No	安定化変換効率	光劣化率	耐熱劣化率	セル耐電圧	歩留り
SC実2	1	1	1	1	1
SC比2	0.92	1.12	1.13	0.97	0.99

[0208] the laminating mold photovoltaic cell (SC fruit 2) of this invention is superior to the conventional laminating mold photovoltaic cell (SC ratio 2) in the photoelectric conversion efficiency after stabilization of a photovoltaic cell (stabilization conversion efficiency), the rate of photodegradation, the rate of heat-resistant degradation, cel withstand voltage, and the yield as mentioned above -- I understand.

[0209] <<example 3>> Although 2nd i type layer 110 which consists of muc-Si in an example 1 forms, the flow rate of SiH<sub>4</sub> gas adjusted with each massflow controllers 456 and 458 so that the flow rate of 70sccm(s) and H<sub>2</sub> gas might serve as 2100sccm(s), and it adjusted opening of a non-illustrated conductance bulb to it so that the pressure in i type layer deposition chamber 418 might become with 0.05Torr.

[0210] Next, 0.15W /of RF power sources 424 was set as 3 cm, and it was impressed by the bias rod 428. Then, the power of a non-illustrated microwave power source (0.5GHz) is set as 0.12 W/cm<sup>3</sup>. Carry out microwave power installation into i type layer deposition chamber 418 through the bias rod 428, and glow discharge is made to occur. Production of 2nd i type layer was started on the 2nd RFn type layer, the output of a stop and bias power supply 424 was cut for glow discharge in the place which produced i type layer of 1.0 micrometers of thickness, and production of 2nd i type layer 110 was finished.

[0211] Eight things to which 2nd i type layer 110 which consists of above-mentioned muc-Si similarly changed only thickness among 0.3-2.0 micrometers were produced, and it measured about initial conversion efficiency, the curvilinear factor, and the rate of photodegradation. The measurement result is shown in Table 3.

[0212]

[Table 3]

第二のi型層の 膜厚 (μm)	0.3	0.5	0.7	1	1.2	1.5	1.8	2.0
初期変換効率	×	○	○	○	○	○	△	△
曲線因子	△	△	○	○	○	○	△	×
光劣化率	△	○	○	○	○	○	△	△

○ : 実用上最適

△ : 実用上十分

× : 実用上不十分

[0213] About initial conversion efficiency, the curvilinear factor, and the rate of photodegradation, thing practically sufficient among 0.5-1.5 micrometers was obtained.

[0214] In the laminating mold photovoltaic cell of this invention, what shows the property in which the thickness of 2nd i type layer 110 which consists of muc-Si excelled in [ 0.5 micrometer or more ] 1.5 micrometers or less was obtained.

[0215] <<example 4>> Although 3rd i type layer 105 which consists of muc-Si in an example 1 forms, the flow rate of SiH<sub>4</sub> gas adjusted with each massflow controllers 456 and 458 so that the flow rate of 80sccm(s) and H<sub>2</sub> gas might serve as 3200sccm(s), and it adjusted opening of a non-illustrated conductance bulb to it so that the pressure in i type layer deposition chamber 418 might become with 0.2Torr(s).

[0216] Next, the power of a non-illustrated microwave power source (0.1GHz) is set as 0.15 W/cm<sup>3</sup>. Carry out microwave power installation into i type layer deposition chamber 418 through the bias rod 428, and glow discharge is made to occur. Production of 3rd i type layer was started on the 3rd RFn type layer, the output of a stop and bias power supply 424 was cut for glow discharge in the place which produced i type layer of 3.0 micrometers of thickness, and production of 3rd i type layer 105 was finished.

[0217] Eight things to which 3rd i type layer 105 which consists of above-mentioned muc-Si similarly changed only thickness among 1.0-4.0 micrometers were produced, and it measured about initial



conversion efficiency, the curvilinear factor, and the rate of photodegradation. The measurement result is shown in Table 4.

[0218]

[Table 4]

第三のi型層の 膜厚 ( $\mu\text{m}$ )	1	1.5	2	2.5	3	3.5	3.8	4.0
初期変換効率	×	○	○	○	○	○	△	×
曲線因子	△	○	○	○	○	○	△	×
光劣化率	△	○	○	○	○	○	△	△

○ : 実用上最適  
△ : 実用上十分  
× : 実用上不十分

[0219] About initial conversion efficiency, the curvilinear factor, and the rate of photodegradation, thing practically sufficient among 1.5-3.5 micrometers was obtained.

[0220] In the laminating mold photovoltaic cell of this invention, 1.5-micrometer or more range of the thickness of third i type layer 105 which consists of muc-Si is 3.5 micrometers or less, and what shows the outstanding property was obtained.

[0221] <<example 5>> although 2nd i type layer 110 which performs similarly formation of 2nd n type layer 108 in an example 1, and consists of muc-Si forms The flow rate of SiH<sub>4</sub> gas adjusts [ 55sccm(s) and H<sub>2</sub> quantity of gas flow ] with each massflow controllers 456 and 458 so that it may be set to 1500sccm(s). Furthermore, the flow rate of B-2H<sub>6</sub>-/H<sub>2</sub> gas was adjusted so that the content of the boron contained in the microcrystal silicon which is 2nd i type layer 110 might be set to 0-10.0 ppm with a massflow controller 460, and the laminating mold photovoltaic cell was produced. n type layers other than the above, i type layer, and p type layer were produced like the example 1.

[0222] In addition, imf-4f made from CAMECA was used for measurement of the content of the boron in 2nd i type layer 110.

[0223] The property the content of the boron contained in silicon excelled [ property ] in 2nd i type layer 110 8.0 ppm or less in initial conversion efficiency, stabilization conversion efficiency, the rates of photodegradation, and all the rates of heat deterioration was acquired. The measurement result is shown in Table 5.

[0224]

[Table 5]

第二のi型層の B含有量 (ppm)	0	1	3	8	10
初期変換効率	○	○	○	△	×
安定化変換効率	○	○	○	△	△
光劣化率	○	○	○	○	△
熱劣化率	○	○	○	○	△

○ : 実用上最適  
△ : 実用上十分  
× : 実用上不十分

[0225] <<example 6>> although 3rd i type layer 105 which performs similarly formation of 3rd n type layer 103 in an example 1, and consists of muc-Si forms The flow rate of SiH<sub>4</sub> gas adjusts with each massflow controllers 456 and 458 so that the flow rate of 45sccm(s) and H<sub>2</sub> gas may serve as 1550sccm (s). Furthermore, the flow rate of B-2H<sub>6</sub>-/H<sub>2</sub> gas was adjusted so that the content of the boron contained in the microcrystal silicon which is 3rd i type layer 105 might be set to 0-10.0 ppm with a massflow controller 460, and the laminating mold photovoltaic cell was produced. n type layers other than the above, i type layer, and p type layer were produced like the example 1.

[0226] In addition, imf-4f made from CAMECA was used for measurement of the content of the boron in 3rd i type layer 105.

[0227] The property the content of the boron contained in silicon excelled [ property ] in 3rd i type layer 105 8.0 ppm or less in initial conversion efficiency, stabilization conversion efficiency, the rates of photodegradation, and all the rates of heat deterioration was acquired. The measurement result is shown in Table 6.

[0228]

[Table 6]

第三のi型層の B含有量 (ppm)	0	1	3	8	10
初期変換効率	○	○	○	△	×
安定化変換効率	○	○	○	△	△
光劣化率	○	○	○	○	△
熱劣化率	○	○	○	○	△

○ : 実用上最適  
△ : 実用上十分  
× : 実用上不十分

[0229] <<example 7>> In the example 1, the laminating mold photovoltaic cell which has the 2nd RFn type layer which newly consists of a-Si between 107 and 108 was produced. Drawing 2 shows the cross-section structure of this laminating mold photovoltaic cell.

[0230] In order to have formed the 2nd RFn type layer which consists of a-Si, in the deposition chamber 417, bulbs 443, 433, 444, and 434 were operated and SiH<sub>4</sub> gas and PH<sub>3</sub>/H<sub>2</sub> gas were introduced through the gas installation tubing 429.

[0231] At this time, the flow rate of SiH<sub>4</sub> gas adjusted with massflow controllers 438, 436, and 439 so that the flow rate of 80sccm(s) and PH<sub>3</sub>/H<sub>2</sub> gas might serve as [ the flow rate of 3sccm(s) and H<sub>2</sub> gas ] 5sccm(s), and it adjusted the pressure in the deposition chamber 417 so that it might be set to 1.0Torr(s).

[0232] Set the power of the RF power source 422 as 0.03 W/cm<sup>3</sup>, introduce RF power into the cup 420 for plasma formation, and glow discharge is made to occur. RF power source was shut off in the place which started formation of the RFn type layer 208 which consists of Si, and formed the 2nd RFn type layer of 10nm of thickness on 207 layers of 3rd p type layer, and formation of the RFn type layer 208 which consists glow discharge of a stop and the 2nd a-Si was finished.

[0233] Evacuation of a stop, the deposition interior of a room, and the inside of gas piping was carried out for the inflow of SiH<sub>4</sub> gas into the deposition chamber 417, PH<sub>3</sub>/H<sub>2</sub> gas, and H<sub>2</sub> gas to 1x10<sup>-5</sup>Torr. Furthermore, n type layer 209 which consists of muc-Si was formed 10nm of thickness like the example 1.

[0234] Other deposits were performed by the same approach as an example 1, and the laminating mold photovoltaic cell as shown in drawing 2 was obtained. Suppose that this photovoltaic cell is called the SC fruit 7.

[0235] <Example 7 of a comparison> RF was used for a-Si and 2nd i type layer for a-Si in 3rd n type layer in an example 1 in a-SiGe and 2nd n type layer at a-Si and 3rd i type layer, respectively, and the laminating mold photovoltaic cell was produced. Suppose that this photovoltaic cell is called the SC ratio 7. Production of p type layers other than the above, i type layer, and n type layer was performed like the example 1. Table 71 shows a quantity of gas flow.

[0236]

[Table 71]

(比7)	SiH <sub>4</sub> 流量 sccm	Si <sub>3</sub> H <sub>8</sub> 流量 sccm	CH <sub>4</sub> 流量 sccm	GeH <sub>4</sub> 流量 sccm	H <sub>2</sub> 流量 sccm	PH <sub>3</sub> /H <sub>2</sub> 流量 sccm	B <sub>2</sub> H <sub>6</sub> /H <sub>2</sub> SiH <sub>4</sub> / 流量 sccm	流量 sccm	压力 Torr	MW 電力 W/cm <sup>2</sup>	RF 電力 W/cm <sup>2</sup>	基板 温度 ℃	層厚 nm
RF n型層	2.2				80	10			1.3		0.05	380	10
RF i型層		3.5			100				0.65		0.008	300	10
MW i型層	48			51	170				0.01	0.1	0.32	380	170
RF i型層		3.5			100				0.65		0.008	300	23
RF p型層			0.1		80		9	3	1.8		0.07	300	10
RF n型層	1.8				70	8			1.2		0.008	320	10
MW i型層	80				350				0.02	0.1	0.205	300	350
RF p型層			0.2		80		9	3	1.7		0.07	260	10
RF n型層	1.1				50	10			1.05		0.04	230	10
RF i型層		2.0			200				0.8		0.007	180	90
RF p型層			0.4		90		8	3	1.6		0.07	170	10

[0237] It produced the SC fruit 7 and six SC ratios 7 at a time, respectively, they performed measurement of stabilization conversion efficiency, the rate of photodegradation, the rate of heat-resistant degradation, cel withstand voltage, and the yield like the example 1 of a comparison, and computed the average. The property of the SC ratio 7 came to be shown in Table 7 to the SC fruit 7 as a result of measurement.

[0238]

[Table 7]

試料No	安定化変換効率	光劣化率	耐熱劣化率	セル耐電圧	歩留り
SC実7	1	1	1	1	1
SC比7	0.88	1.20	1.15	0.99	0.99

[0239] Thus, it turned out that the laminating mold photovoltaic cell (SC fruit 7) of this invention is

superior to the conventional laminating mold photovoltaic cell (SC ratio 7) in stabilization conversion efficiency, the rate of photodegradation, the rate of heat-resistant degradation, cel withstand voltage, and the yield.

[0240] <<example 8>> by the approach as production of muc-Si layer of 110 of the second pin junction in an example 1 with i same layers After examining the production conditions from which the light absorption multiplier of 950nm differs by changing a hydrogen dilution ratio, substrate temperature, etc. beforehand, Four laminating mold photovoltaic cells from which the light absorption multiplier of 950nm differs using the above-mentioned production conditions at the time of production of muc-Si layer of i type layer 110 of the second pin junction in an example 1 were produced. And the same evaluation as an example 1 was performed. The evaluation result is shown in Table 8.

[0241]

[Table 8]

第二のi型層の 950nmの光吸収 係数 (cm <sup>-1</sup> )	≤ 10	100	200	400
初期変換効率	×	×	○	○
安定化変換効率	×	△	○	○
光劣化率	×	×	○	○
熱劣化率	×	△	○	○

○ : 実用上最適  
△ : 実用上十分  
× : 実用上不十分

[0242] Thus, by making or more [ 200cm - ] into one the light absorption multiplier of 950nm of the microcrystal silicon which is i type layer of the second pin junction of the laminating mold photovoltaic cell (SC fruit 8) of this invention showed having the property which was excellent in initial conversion efficiency, stabilization conversion efficiency, the rates of photodegradation, and all the rates of heat-resistant degradation.

[0243] <<example 9>> by the approach as production of muc-Si layer of 105 of the third pin junction in an example 1 with i same layers After examining the production conditions from which the light absorption multiplier of 950nm differs by changing a hydrogen dilution ratio, substrate temperature, etc. beforehand, Four photovoltaic cells from which the light absorption multiplier of 950nm differs using the above-mentioned production conditions at the time of production of muc-Si layer of i type layer 105 of the third pin junction in an example 1 were produced. And the same evaluation as an example 1 was performed. The evaluation result is shown in Table 9.

[0244]

[Table 9]

第三のi型層の 950nmの光吸収 係数 (cm <sup>-1</sup> )	≤ 10	100	200	400
初期変換効率	×	×	○	○
安定化変換効率	×	×	○	○
光劣化率	×	△	○	○
熱劣化率	×	△	○	○

○ : 実用上最適  
△ : 実用上十分  
× : 実用上不十分

[0245] Thus, by making or more [ 200cm - ] into one the light absorption multiplier of 950nm of the microcrystal silicon which is i type layer of the third pin junction of the laminating mold photovoltaic cell (SC fruit 9) of this invention showed having the property which was excellent in initial conversion efficiency, stabilization conversion efficiency, the rates of photodegradation, and all the rates of heat-resistant degradation.

[0246] <<example 10>> The deposition equipment using a roll-to-roll process as shown in drawing 5

was used, and the photovoltaic cell of the triple mold shown in drawing 3 was produced. In drawing 5, it is the roll-like substrate with which 5010 is arranged at a load room and 5400 is arranged at a load room, and is the rolling-up fixture with which 5150 is arranged at an unload room and 5042 is arranged at an unload room.

[0247] As for first n type layer deposition room and 5130, 5120 is [ the first RF-i type layer (p/i) deposition room and 5140 ] first p type layer deposition room. Moreover, as for second n type layer deposition room and 5090, 5070 is [ the second MW-i type layer deposition room and 5110 ] second p type layer deposition room. Furthermore, for 5020 and 5030, as for the third MW-i type layer deposition room and 5050, third n type layer deposition room and 5040 are [ the third RF-i type layer (p/i) deposition room and 5060 ] third p type layer deposition room.

[0248] 5011, 5021, 5031, 5041, 5051, 5061, 5071, 5091, 5111, 5121, 5131, 5141, and 5151 are exhaust pipes, and 5012, 5022, 5032, 5042, 5052, 5062, 5072, 5092, 5112, 5122, 5132, 5142, and 5152 are the exhaust air pumps connected to the exhaust pipe.

[0249] 5201-5214 are the gas gates and 5301-5314 are gas supply lines. Moreover, 5025, 5035, 5045, 5055, 5065, 5075, 5095, 5115, 5125, 5135, and 5145 are material gas supply pipes, and 5026, 5036, 5046, 5056, 5066, 5076, 5096, 5116, 5126, 5136, and 5146 are mixing equipment of material gas.

[0250] 5024, 5034, 5054, 5064, 5074, 5114, 5124, 5134, and 5144 are RF power sources, and 5023, 5033, 5053, 5063, 5073, 5113, 5123, 5133, and 5143 are the coaxial cables for RF supply. Moreover, 5044 and 5094 are MW power sources and 5043 and 5093 are the waveguides for MW installation.

[0251] The sheet-like substrate which has die length of 300m, width of face of 30cm, and a thickness 0.2mm band-like light reflex layer was used for the substrate.

[0252] Next, the sheet-like substrate which has the light reflex layer in which the triple mold photovoltaic cell shown in drawing 3 was formed was set to the load room 5010 for sheet-like substrate installation using the photovoltaic-cell formation equipment of the roll two roll method shown in drawing 5. Table 101 shows the formation conditions of a triple mold photovoltaic cell.

[0253]

[Table 101]

(表10)	SiH <sub>4</sub> 流量 sccm	Si <sub>3</sub> H <sub>8</sub> 流量 sccm	CH <sub>4</sub> 流量 sccm	GeH <sub>4</sub> 流量 sccm	H <sub>2</sub> 流量 sccm	PH <sub>3</sub> /H <sub>2</sub> 流量 sccm	B <sub>2</sub> H <sub>6</sub> /H <sub>2</sub> 流量 sccm	SiH <sub>4</sub> /H <sub>2</sub> 流量 sccm	压力 Torr	MW 電力 W/cm <sup>2</sup>	RF 電力 W/cm <sup>2</sup>	基板 温度 ℃	層厚 nm
RF n型層	2.2				75	10			1.3		0.05	380	10
RF n型層	0.2				100	5			0.65		0.1	290	13
MW i型層	48				1600				0.05	0.10	0.32	300	3000
RF i型層		4.0			100				0.65		0.008	290	23
RF p型層			0.1		80		9	4	1.8		0.08	300	10
RF n型層	0.2				150	8			0.7		0.08	320	100
MW i型層	80				1300				0.1	0.15	0.12	300	1000
RF p型層			0.2		80		9	4	1.7		0.08	260	10
RF n型層	1.1				50	10			1.05		0.04	220	10
RF i型層		2.0			200				0.8		0.007	180	80
RF p型層			0.4		90		8	3	1.6		0.08	160	10

[0254] The sheet-like substrate was connected to the sheet rolling-up fixture of the unload room 5150 through all the deposition interior of a room and all the gas gates. Each deposition room was exhausted to 10 to 3 or less Torrs with the non-illustrated exhaustor. Desired material gas was supplied to each deposition room from the mixing equipments 5026, 5036, 5046, 5056, 5066, 5076, 5096, 5116, 5126, 5136, and 5146 for each deposition film formation. And gas was supplied to each gas gates 5201-5214 from each gate gas transfer unit.

[0255] After having heated the substrate at the heater for substrate heating of each deposition equipment, adjusting whenever [ closing motion / of the exhaust air bulb of each exhaustor ], adjusting to the degree of vacuum and stabilizing substrate temperature and a degree of vacuum, conveyance of a sheet-like substrate was begun and RF power for plasma generating and microwave (frequency: 0.5GHz, 2.45GHz) power were supplied to each deposition room.

[0256] The triple mold photovoltaic cell which carried out 3 laminatings of the pin structure of drawing

3 on 100m of sheet-like substrates as mentioned above was produced. Moreover, microwave (0.5GHz) was used for formation of 2nd i type layer, and microwave (2.45GHz) was used for formation of 3rd i type layer.

[0257] Next, vacuum deposition of the ITO of 70nm of thickness was carried out with the vacuum deposition method as a transperence conductive layer 115 on the RFp type layer 114.

[0258] And the mask which the hole of a tandem type opened was carried on the transperence conductive layer 115, and vacuum deposition of the current collection electrode 116 of Kushigata which consists of Cr(40nm)/Ag(1000nm)/Cr (40nm) was carried out with the vacuum deposition method. Above, production of a laminating mold photovoltaic cell was finished. Suppose that this photovoltaic cell is called the SC fruit 10.

[0259] <Example 10 of a comparison> on the substrate which produced the light reflex layer on the same conditions as an example 10 Like the example 1 of a comparison, the 3rd RFn type layer, i type layer, a MWi type layer, a RFi type layer, p type layer, the 2nd RFn type layer, i type layer, p type layer, the 1st RFn type layer, i type layer, and p type layer were produced, and the laminating mold photovoltaic cell which used a-Si for the 2nd RFn type layer at a-Si and 2nd i type layer was produced. Suppose that this photovoltaic cell is called the SC ratio 10.

[0260] It produced the SC fruit 10 and eight SC ratios 10 at a time, respectively, they performed measurement of stabilization conversion efficiency, the rate of photodegradation, the rate of heat-resistant degradation, cel withstand voltage, and the yield, and computed the average. The property of the SC ratio 10 came to be shown in Table 10 to the SC fruit 10 as a result of measurement.

[0261]

[Table 10]

試料No.	安定化変換効率	光劣化率	耐熱劣化率	セル耐電圧	歩留り
SC実10	1	1	1	1	1
SC比10	0.89	1.21	1.14	0.99	0.98

[0262] Thus, the conventional laminating mold photovoltaic cell (SC ratio 10) showed having the property in which the laminating mold photovoltaic cell (SC fruit 10) of this invention was excellent in stabilization conversion efficiency, the rate of photodegradation, the rate of heat-resistant degradation, cel withstand voltage, and the yield.

[0263]

[Effect of the Invention] according to [ as explained above ] this invention -- as i type layer of the second pin junction -- microcrystal silicon -- using -- as i type layer of the third pin junction -- microcrystal silicon -- \*\*\*\* -- in the laminating mold photovoltaic cell of an amorphous system, an improvement of the semi-conductor layer whose photodegradation was large is made by things, and photodegradation can especially be controlled also in a laminating mold photovoltaic cell by them.

[0264] Moreover, by using microcrystal silicon as an i type layer of the third pin junction, light absorption also of the comparatively difficult long wavelength light can be carried out, it has the higher short-circuit current and the open end electrical potential difference also in the photovoltaic cell of a stack mold, and carrying out light absorption until now can maintain high photoelectric conversion efficiency.

[0265] Furthermore, by separating from the thickness considered to be conventionally suitable in the thickness of the microcrystal silicon which is i type layer of the second pin junction, or/and the thickness of the microcrystal silicon which is i type layer of the third pin junction, and making it thin, the increment in the localized level in the inside of i type layer by optical exposure can be controlled, and photodegradation can especially be controlled also in a laminating mold photovoltaic cell.

[0266] And the thing for which boron is contained in the microcrystal silicon which is i layers of the second pin junction, and the content is set to 8 ppm or less, Or/and, by containing boron in the microcrystal silicon which is i type layer of the third pin junction, and setting the content to 8 ppm or less High photoelectric conversion efficiency is maintainable by not checking growth of microcrystal



silicon and its microcrystal, and improving the performance traverse of the hole at the time of an optical generation of electrical energy, controlling photodegradation.

[0267] Moreover, by forming n type layer of the second pin junction from the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon Or/and, by forming n type layer of the third pin junction from the bilayer of microcrystal silicon or microcrystal silicon, and amorphous silicon The microcrystal silicon or the microcrystal of i type layer formed on n type layer can be formed by the quick rate of sedimentation, good microcrystal silicon with few impurities can be formed, photodegradation can be lessened, and high photoelectric conversion efficiency can be maintained.

[0268] Furthermore, by having formed the microcrystal silicon which is i type layer of the second and third pin junction by the microwave plasma-CVD method, and having made or more [ 200cm - ] into one the light absorption multiplier of 950nm of the microcrystal silicon which is i type layer By separating from the thickness considered to be conventionally suitable in the thickness of the microcrystal silicon which is i type layer of the second and third pin junction, and making it thin The increment in the localized level in the inside of i type layer by optical exposure can be controlled, and photodegradation can especially be controlled also in a laminating mold photovoltaic cell. Moreover, carrying out light absorption until now can also absorb the light of the comparatively difficult long wavelength, and the higher photoelectric conversion efficiency also in a laminating mold photovoltaic cell can be maintained.

[0269] And if the laminating mold photovoltaic cell of this invention is formed with a roll-to-roll process, productivity can be raised extremely.

[0270] Thus, according to the laminating mold photovoltaic cell of this invention, photodegradation can be controlled, the rate of photodegradation can be reduced, maintaining high photoelectric conversion efficiency, and the conversion efficiency after photodegradation can be raised. By it, though it is the low cost suitable for practical use, dependability can offer a photovoltaic cell with high photoelectric conversion efficiency highly.

[0271] Moreover, according to this invention, by having used microcrystal silicon for i type layer of the second pin junction, and having used microcrystal silicon for i type layer of the third pin junction, the yield like the withstand voltage of the whole photovoltaic cell, heat-resistant degradation, and a manufacture line can improve, and the flexibility of the use gestalt of a photovoltaic cell can be raised.

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[Translation done.]